Part of the far-infrared laser magnetic resonance spectrum of the $\text{HF}^+$ free radical

Michael D. Allen,a,1 Kenneth M. Evenson,a,2 and John M. Brown,b,*

a Time and Frequency Division, NIST, 325 Broadway, Boulder, CO 80305, USA
b The Physical and Theoretical Chemistry Laboratory, The Chemistry Department, South Parks Road, Oxford OX1 3QZ, UK

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Abstract

Transitions between the spin-rotational levels of the $\text{HF}^+$ radical in the $\epsilon = 0$ level of the $\text{X}^1\Sigma^+$ ground state have been observed by the technique of laser magnetic resonance at far-infrared wavelengths. Because of the large spin–orbit coupling in this $\text{H}^1\Sigma^+$ state, the detection of the fine-structure transitions required the use of very short-wavelength laser lines (down to 40 μm). These observations have provided accurate information on the $\text{H}^1\Sigma^+$ fine-structure splittings in rotational levels of the upper $\text{H}^1\Sigma^+$ spin component for the first time which has enabled the complete determination of the hyperfine structure for this molecule. An effective Hamiltonian was used to model the experimental measurements; this provided considerably more accurate values for the various molecular parameters than previously available. Using these parameters, predictions of the transition frequencies between the low-lying spin-rotational levels of the radical are of great importance and have been made.

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1. Introduction

The $\text{HF}^+$ radical is iso-electronic with OH (and also NH). It therefore comes as something of a surprise to discover that it has been comparatively little studied by spectroscopists. Fowle et al. [1] were the first to observe the $m$-isotopic, using photodetachment spectroscopy of HF. These results were improved upon and corrected soon afterwards by Brandt [2]. He was able to determine the vertical ionisation energies to the $\text{X}^1\Sigma^+$ and $\text{A}^1\Sigma^+$ excited states of HFH and the approximate vibrational intervals in these states. These values were further refined in subsequent photo-ionisation [3] and photoelec-

tron [4] experiments at higher resolution; it was even possible to resolve the spin–orbit splitting in the $\text{X}^1\Sigma^+$ state by detecting the threshold electrons [5]. At about the same time, Gewurtz et al. [6] recorded the emission spectrum associated with the weak $\text{A}^3\Sigma^+–\text{X}^3\Sigma^+$ electronic transition at rotational resolution. They determined values for many of the important properties of the ion, including the dissociation limit of the weakly bound $\text{D}^2\Sigma^+$ state. A few years later, part of the rotational spectrum of $\text{HF}^+$ in the ground state was recorded by Hovde et al. [7] using the technique of laser magnetic resonance (LMR) at far-infrared wavelengths. This study revealed the rather large hyperfine splittings associated with the $\text{H}^1\Sigma^+$ nuclear ground state. For these studies, the $\text{H}^1\Sigma^+$ state is of considerable interest because it is the ground state of the $\text{H}^2\Sigma^+$ spin component. The final piece of the experimental information on $\text{HF}^+$ was provided by Hovde et al. [8] who recorded some $R$-lines in the fundamental band of the vibration–rotation spectrum at about 2912 cm⁻¹; they used velocity modulation to detect the signals. This produced a more accurate measurement of the vibrational interval and also revealed a possible $\text{A}^3\Sigma^+$ hyperfine structure on some of the $\text{R}^2\Sigma^+$ transitions. $\text{HF}^+$ has also been the subject of some theoretical calculations. These have been concerned with the electronic structure of the molecule in its lowest electronic states [9,10], the lambda-doubling intervals [11,12], and nuclear hyperfine structure [13]; both the latter refer to the molecule in the $\text{X}^1\Sigma^+$ state.

* Corresponding author. Fax: +44-1865-275410.
Email address: jonb@physchem.ox.ac.uk (J.M. Brown).

1 Present address: Kilnside, 3100 Logic Drive, Longmont, CO 80503, USA.

2 Ken Fowle died on 29 January 2002.
The major advance in far-infrared spectroscopy in recent years has been a push to shorter wavelengths, into the "true" far-infrared region below 100 μm. This has enabled the detection of pure rotational transitions of very light molecules [14], fine-structure transitions in both atomic [15] and molecular [16] and even some vibrational transitions of low-frequency bending vibrations [17]. One limitation of the earlier high-resolution studies of HF* in the X'1Π state was that they provided rather sparse information in the molecule in the upper, A'2Π spin component. These levels lie some 310 cm⁻¹ above those of the lower component and are by comparison rather sparsely populated. In addition, the molecule has a very small magnetic moment in these upper levels which hinders its study by magnetic resonance methods. Information on the A'2Π levels is needed for a complete determination of the molecular parameters of HF* (for example, there are four hyperfine parameters for each nuclear spin of the A'2Π levels give direct information on only one of them). The availability of new, short-wavelength far-infrared laser lines brings the fine-structure transitions of HF* into range and so gives access to these levels.

In this paper, we report a limited study of the fine-structure transitions of HF* in the v = 0 level of the X'1Π state by LMR together with an extension of the pure rotational transitions in the A'2Π component. These measurements are sufficient to provide a complete determination of the molecular parameters for this molecule with a considerable improvement in accuracy. The bond length of the molecule has been refined as a result. The HF* hyperfine parameters obtained make an interesting comparison with those predicted by theory [13].

2. Experimental details

The far-infrared LMR experiments were performed at the Boulder laboratories of NIST; the spectrometer has been described in detail elsewhere [18]. The HF* radicals were produced in the spectrometer sample volume by flowing a lean mixture of HF in helium through a special microwave discharge designed so that the resultant plasma projected out into the laser radiation field. A similar microwave discharge source has been described briefly in our earlier study of OH* [19]. The total pressure in the sample volume was about 0.4 Torr (55 Pa). The HF gas was dried with liquid nitrogen and bled into the discharge at a rate which did not register on the pressure gauge (less than 2 nm Torr). The far-infrared radiation was coupled out of the laser cavity and detected with a liquid helium-cooled gallium-germanium photo-conductor. The magnetic field was modulated at a frequency of 39 kHz and the signal detected with a lock-in amplifier at the same frequency. The resonances were subsequently displayed as the first derivative of an absorption profile. The magnet of the LMR system was controlled by a rotating-coil magnetometer which provided a direct readout of the flux densities. The system was calibrated periodically up to 1.8 T with a proton NMR gaussmeter; the absolute uncertainty of measurement was 10⁻⁴ T below 1.1 T and the fractional uncertainty was 10⁻¹ above 0.1 T.

3. Results and analysis

3.1. Observations and assignments

The far-infrared transitions of HF* in the v = 0 level which have been detected in the LMR experiment are summarized in Table 1; they are also shown on an energy level diagram in Fig. 1. All together, resonances associated with five separate rotational and fine-structure transitions have been observed. An example from the 87.73 μm spectrum is shown in Fig. 2; the transition involved in J = 7/2 → 5/2, M_J = 3/2 → -5/2 in the A'2Π component. The HF* nuclear hyperfine interaction is responsible for the small doubling of each line in this spectrum while the corresponding interaction involving the 13C nucleus produces a much larger doublet splitting of about 100 μm (both nuclei have J = 1/2). A second example in Fig. 3 shows a single Zeeman component of the J = 5/2 → 3/2 fine-structure transition, recorded with the 44.24 μm line. The HF* resonance corresponds to one of the two 13C hyperfine doublets; its companion lies to higher field beyond the end of the region shown. The line shows a just-resolvable 13C doubling when recorded more slowly over a narrower field range. It can be seen by comparison of Fig. 3 with 2 that the fine-structure transitions (which are electric-dipole in character) are much weaker than the pure rotational transitions. The spectra recorded with short-wavelength laser lines all show the presence of several "impurity" species in the discharge, despite the simplicity of the production method. One of these is, of course, the OH radical in its X'1Π state. It produces strong signals on the 124.4 μm line (J = 7/2 → 5/2) in the A'2Π component of the v = 1 level, the 87.73 μm line (J = 7/2 → 5/2) in the A'2Π component of the v = 1 level, and the 48.74 μm line (J = 7/2 → 9/2, A'2Π → X'1Π) fine-structure transition in the v = 0 level. Part of the 87.73 μm spectrum is shown in Fig. 2. Several unidentified signals remain. Three are shown in Fig. 3 where it can be seen that some of them are very strong. The two signals marked B appear to be related. If the splitting of 180 mT between them corresponds to a hyperfine interaction, it strongly suggests that the molecule concerned contains a fluorine atom. Further investigation of these intriguing observations is being undertaken.

The detailed measurements of the individual resonances for the six laser lines used to record LMR spectra are given in Table 2. The assignments were made with the help of a computer program which predicts all possible resonances for a given laser frequency, together with their lines strengths and tuning rates [20,21]. This information constitutes the Zeeman pattern which can be used to make the assignments even when the

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Table 1

Summary of observations in the far-infrared spectrum of HF* in the v = 0 level of its X'1Π state

<table>
<thead>
<tr>
<th>HF* transitions observed</th>
<th>Laser line</th>
<th>ν (GHz)</th>
<th>Gas</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational transitions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9/2 → 7/2</td>
<td>± +</td>
<td>124.4</td>
<td>CH_3OH</td>
<td>108(20)</td>
</tr>
<tr>
<td>9/2 → 5/2</td>
<td>± +</td>
<td>122.5</td>
<td>CH_3OH</td>
<td>108(20)</td>
</tr>
<tr>
<td>7/2 → 5/2</td>
<td>± -</td>
<td>87.73</td>
<td>C_2H_5OH</td>
<td>108(38)</td>
</tr>
<tr>
<td>Fine-structure transitions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/2 → 3/2</td>
<td>± +</td>
<td>48.72</td>
<td>C_2H_5OH</td>
<td>90(6)</td>
</tr>
<tr>
<td>1/2 → 1/2</td>
<td>± ±</td>
<td>48.24</td>
<td>C_2H_5OH</td>
<td>90(6)</td>
</tr>
<tr>
<td>1/2 → 1/2</td>
<td>± -</td>
<td>39.92</td>
<td>C_2H_5OH</td>
<td>90(6)</td>
</tr>
</tbody>
</table>

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Fig. 1. Diagram showing the lower energy levels of the HF* radical in the v = 0 level of the X'1Π state and the transitions involved in the observed far-infrared LMR spectrum. The lambda-type (parity) doubling has been exaggerated by a factor of 30 for the sake of clarity.

Fig. 2. Part of the far-infrared LMR spectrum of the HF* radical in the v = 0 level of the X'1Π state. The spectrum is recorded with the 87.73 μm laser line in perfluorodecalin solution (ΔM_J = ±1). The rotational transition involved in J = 7/2 → 5/2, M_J = 3/2 → -5/2, ν = 108.2 GHz. The 13C and 14N hyperfine structures are both fully resolved; the nuclear spin selection rule is ΔM_J = 0 (see Table 2). This scan also shows one of the OH impurity lines resulting from the microwave discharge (slightly damped) HF in helium. In this case, the OH is vibrationally excited, in the v = 1 level.
The major advance in far-infrared spectroscopy in recent years has been a push to shorter wavelengths, into the "true" far-infrared region below 100 μm. This has enabled the detection of pure rotational transitions of very light molecules [14], fine-structure transitions in both atoms [15] and molecules [16] and even some vibration–rotation transitions for low-frequency bending vibrations [17]. One limitation of the earlier high resolution studies of HD in 2e μm [18] was that they provided rather little information on the molecule in the upper, 2H/2 spin component. These levels lie some 310 cm⁻¹ above those of the lower component and are by comparison rather sparsely populated. In addition, the molecule has a very small magnetic moment in these upper levels which hinders their study by magnetic resonance methods. Information on the 2H/2 levels is needed for a complete determination of the molecular parameters of HD [19] (for example, there are four hyperfine parameters for each nuclear spin but studies of the 2H/2 levels give direct information on only one of them). The availability of new, short-wavelength far-infrared laser lines brings the fine-structure transitions of HD into range and so gives access to these levels.

In this paper, we report a limited study of the fine-structure transitions of HD in the ν = 0 level of the X(2S) state by LMR together with an extension of the pure rotational transitions in the 2H/2 component. These measurements are sufficient to provide a complete determination of the molecular parameters for this molecule with a considerable improvement in accuracy. The bond length of the molecule has been refined as a result. Of the 19 HD hyperfine parameters obtained make an interesting comparison with those predicted by theory [13].

2. Experimental details

The far-infrared LMR experiments were performed at the Boulder Laboratories of NIST; the spectrometer has been described in detail elsewhere [18]. The HD⁺ radicals were produced in the spectrometer sample volume by flowing a lean mixture of HD in helium through a special microwave discharge designed so that the resultant plasma is projected out into the laser radiation field. A similar microwave discharge source has been described briefly in our earlier study of OH⁺ [19]. The total pressure in the sample volume was about 0.4 Torr (55 Pa). The HD⁺ gas was dried with liquid nitrogen and bled into the discharge at a rate which did not register on the pressure gauge (less than 2 nTorr). The far-infrared radiation was coupled out of the laser cavity and detected with a liquid helium-cooled gallium-germanium photo-conductor. The magnetic field was modulated at a frequency of 39 kHz and the signal detected with a lock-in amplifier at the same frequency. The resonances were consequently displayed as the first derivative of an absorption profile. The magnet of the LMR system was controlled by a rotating-magnet magnetometer which provided a direct readout of the flux densities. The system was calibrated periodically up to 1.8 T with a proton NMR gaussmeter; the absolute uncertainty of measurement was 10⁻⁵ T and the fractional uncertainty was 10⁻⁴ above 0.1 T.

3. Results and analysis

3.1. Observations and assignments

The far-infrared transitions of HD⁺ in the ν = 0 level which have been detected in the LMR experiment are summarized in Table 1; they are also shown on an energy level diagram in Fig. 1. All together, resonances associated with five separate rotational and fine-structure transitions have been observed. An example from the 87.73 μm spectrum is shown in Fig. 2, the transition involved is J = 7/2 → 5/2, Mₗ = 3/2 → 1/2 in the 2H/2 component. The HD⁺ nuclear hyperfine interaction is responsible for the small doubling of each line in this spectrum while the corresponding interaction involving the HD⁻ nucleus produces a much larger doublet splitting of about 100 μm (both nuclei have J = 1/2). A second example in Fig. 3 shows a single Zeeman component of the J = 5/2 → 3/2 fine-structure transition, recorded with the 44.24 μm line. The HD⁺ resonance corresponds to one of the two HD⁺ hyperfine doublets; its companion lies to higher field beyond the end of the region shown. The line shows a just resolvable HD⁺ doubling when recorded more slowly over a narrower field range. It can be seen by comparison of Fig. 3 with 2 that the fine-structure transitions (which are electric-dipole in character) are much weaker than the pure rotational transitions. The spectra recorded with short-wavelength laser lines all show the presence of several "multiplet" species in the discharge, despite the simplicity of the production method. One of these is, of course, the OH radical in its X(2S) state. It produces strong signals on the 1244 μm line (J = 5/2 → 3/2 in the 2H/2 component of the ν = 1 level), the 67.73 μm line (J = 7/2 → 5/2 in the 2H/2 component of the ν = 1 level), and the 48.72 μm line (J = 1/2 → 9/2, 2H/2→2H⁺ fine-structure transitions in the ν = 0 level). Part of the 87.73 μm spectrum is shown in Fig. 2. Several unidentified signals remain. Three are shown in Fig. 3 where it can be seen that some of them are very strong. The two signals marked B appear to be related. If the splitting of 180 μm between these corresponds to a hyperfine interaction, it strongly suggests that the molecule concerned contains a fluorine atom. Further investigation of these intriguing observations is being undertaken.

The detailed measurements of the individual resonances for the six laser lines used to record LMR spectra are given in Table 2. The assignments were made with the help of a computer program which predicts all possible resonances for a given laser frequency, together with their line strengths and tuning rates [20,21]. This information constitutes the Zeeman pattern which can be used to make the assignments even when the

Table 1

<table>
<thead>
<tr>
<th>HD⁺ Transitions Observed</th>
<th>Energy (cm⁻¹)</th>
<th>Giss</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>Parity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/2→3/2</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/2→5/2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9/2→7/2</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fine-structure Transitions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/2→3/2</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/2→1/2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/2→3/2</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/2→5/2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Diagram showing the lower energy levels of the HD⁺ radical in the ν = 0 level of the X(2S) state and the transitions involved in the observed far-infrared LMR spectrum. The lambdada-type (parity) doubling has been exaggerated by a factor of 20 for the sake of clarity.

Fig. 2. Part of the far-infrared LMR spectrum of the HD⁺ radical in the ν = 0 level of the X(2S) state. The spectrum is recorded with the 87.73 μm laser line in perpendicular polarization (ΔMₑ = +1). The rotational transition involved J = 7/2 → 5/2, Mₑ = 3/2 → 1/2. The HD⁺ and HD hyperfine structures are both fully resolved; the nuclear spin selection rule is ΔMₑ = 0 (see Table 2). This scan also shows one of the OH impurity lines resulting from the microwave discharge through (slightly damped) HD in helium. In this case, the OH is vibrationally excited, in the ν = 1 level.
molecular parameters employed are not quite accurate. Fortunately, reasonably reliable values for the molecular parameters of HFP were available from previous workers [6,8]. The resultant assignments are also given in Table 2. The quantum numbers used to describe the molecular states are J, G, parity, M_J, M_G, and M_P, where J and G refer to the 1H and 31P nuclei, respectively. The nuclear spin-de-coupled description is the appropriate one for experiments performed in a magnetic field. An estimate of the experimental uncertainty of each observation is given in the Table. Normally, we would expect some uncertainty to be dominated by the accuracy of the far-infrared laser frequencies which are re-settable to \sqrt{2} x 10^{-5}\nu. However, the modelling of the data with an effective Hamiltonian (see below) did not support this estimate; it seemed to underestimate the reliability of the higher frequency spectra. We have here given each measurement an uncertainty of 2 MHz instead.

3.2. Determination of molecular parameters

A nearly complete set of molecular parameters for HFP in the n = 0 level of its X'II state was determined by fitting a model Hamiltonian to the present measurements by least-squares methods. The effective Hamiltonian was cast in the N^2 form as described by Brown et al. [22] with the Zeeman terms as described in [23]. The eigenstates were identified in terms of the Hund's case (a) quantum numbers given above. The basis set was truncated at states with \Delta J = \pm 2 which reproduced the exact calculations to within a few kHz for the highest field resonances. Each datum was weighted in the fit inversely as the square of its experimental error, estimated to be 2 MHz as given in Table 2. The parameter A_0 was constrained to zero in the fit as a result of which the parameters A_0, \gamma_1, and \gamma_2 are effective parameters [24].

The result of the least-squares fit is given in Table 2; the parameters determined in the process are given in Table 3 in both MHz and cm^{-1} units. Some of the smaller parameters (\theta, \eta, \varphi, \rho, \varphi') have been constrained to values estimated from other sources, using the following relationships [23,25,26]:

\[ H_0 = H_\theta = (2/3)H_\nu \cdot \{12(H_\nu/\omega_0)^2 - \omega_0/\omega_0\}. \]  

(1)

\[ \varphi = -4\Delta H/\nu_0. \]  

(2)

\[ \rho = \rho/2\Delta H. \]  

(3)

\[ \varphi' = -\omega/\nu_0. \]  

(4)

The values adopted are given in Table 3. In addition, the electron spin g-factor was fixed to a value of 2.0023, which corresponds to a relativistic correction of 1.5 x 10^{-5}. It can be seen from Table 2 that the 1H hyperfine splittings were not resolved for most of the fine-structure transitions because, there is very little information on the proton hyperfine interaction for the X'II levels. It was therefore only possible to determine one of the four proton hyperfine parameters in the fit.
molecular parameters employed are not quite accurate. Fortunately, reasonably reliable values for the molecular parameters of HfF₂ were available from previous workers [6,8]. The resultant assignments are also given in Table 2. The quantum numbers used to describe the molecular states are J, \( \Omega \), parity, \( M_J \), \( M_{\Omega} \), and \( M_\Omega \), where \( \Omega_1 \) and \( \Omega_2 \) refer to the \( \text{Hf}^\text{19} \) and \( \text{Hf}^\text{17} \) nuclei, respectively. The nuclear spin-de-coupled description is the appropriate one for experiments performed in a magnetic field. An estimate of the experimental uncertainty of each observation is given in the Table. Normally, we would expect this uncertainty to be dominated by the accuracy of the far-infrared laser frequencies which are re-settable to \( \sqrt{2} \times 10^{-11} \). However, the modeling of the data with an effective Hamiltonian (see below) did not support this estimate; it seemed to underestimate the reliability of the higher frequency spectra. We have therefore given each measurement an uncertainty of 2 MHz instead.

3.2. Determination of molecular parameters

A nearly complete set of molecular parameters for \( \text{HF}^\text{19F} \) in the \( v = 0 \) level of its \( \text{X}^\text{1}\Pi \) state was determined by fitting a model Hamiltonian to the present measurements by least-squares methods. The effective Hamiltonian was cast in the \( \text{N}^\text{1} \) form as described by Brown et al. [22], with the Zeeman terms as described in [23]. The eigenvalues were identified in terms of the Hund's case (a) quantum numbers given above. The basis set was truncated at states with \( \Delta \Omega = \pm 2 \) which reproduced the exact calculations to within a few kHz for the highest field resonances. Each datum was weighted in the fit inversely as the square of its experimental error, estimated to be 2 MHz as given in Table 2. The parameter \( A_\Omega \) was constrained to zero in the fit as a result of which the parameters \( A_\Omega \) and \( \gamma \) are effective parameters [24].

The result of the least-squares fit is given in Table 2; the parameters determined in the process are given in Table 3 in both MHz and cm⁻¹ units. Some of the smaller parameters (\( H_{40}, H_{50}, \gamma \)) have been constrained to values estimated from other sources, using the following relationships [23,25,26]:

\[ H_\Omega = H_\Omega \approx (2/3)D_\Omega \{12(B/\alpha)^2 - z_\alpha/\alpha\}, \]  
(1)

\[ \alpha = -(4D/3B), \]  
(2)

\[ \gamma' = (\gamma / B), \]  
(3)

\[ \gamma'' = (-q / B). \]  
(4)

The values adopted are given in Table 3. In addition, the electron spin- \( g \)-factor was fixed to a value of 2.0020, which corresponds to a relativistic correction of \( 1.5 \times 10^{-3} \). It can be seen from Table 2 that the \( \text{Hf}^\text{19} \) hyperfine splittings were not resolved for most of the fine-structure transitions, consequently, there is very little information on the proton hyperfine interaction for the \( \text{X}^\text{1}\Pi \) levels. It was therefore only possible to determine one of the four proton hyperfine parameters in the fit.
4. Discussion

Although the measurements of the far-infrared LMR spectrum of HF$^+$ in the $v = 0$ level of its $^3\Sigma^+$ state are not very extensive, they have allowed the determination of an essentially complete set of molecular parameters in the effective Hamiltonian, including the $^{3}\Pi$ hyperfine parameters. The values determined are also significantly more reliable than those obtained previously by optical spectroscopy [9] and by a combination of far-infrared LMR and infrared spectroscopy [8], as shown in Tables 4 and 5. Using our values for the ground state parameters and the value for $\gamma_{e}$ we have used for $\gamma_{e}(\gamma_{e})$, 0.0142 cm$^{-1}$ determined by Gewurz et al. [6], we have refit the infrared measurements of Hovde et al. [8] to determine a value for $\gamma_{e}(\gamma_{e})$ of 0.0844(11) cm$^{-1}$. This can be compared with our value for $\gamma_{e}$ to determine the value for the rotational constant at equilibrium, $B_{e}$ = 17.55782 (11) cm$^{-1}$. This in turn corresponds to a value for $\kappa_{e}$ of 0.00959 (12) A that is quoted with a value of 0.0101665 (32) A that the quoted error is purely statistical. This equilibrium bond length is significantly longer than that of HF in its ground state (0.9619 A [29]). The lambda-doubling parameters are also much better determined, particularly the combination of $\gamma_{e}$ and $\gamma_{e}$ (see Table 4). The present study gives values for $p$ and $q$ of 0.9594 and $-0.0640$ cm$^{-1}$ respectively. Hutton and Cooper [12] have made an accurate ab initio calculation of these parameters; for comparison, their values for $p$ and $q$ are -0.57(15) cm$^{-1}$ and -0.15(15) cm$^{-1}$, respectively. A more sensitive feature of their calculation was the inclusion of the effects of the potential curves, which for the ground state as well as for the excited state, the continuum of vibrational levels above the weakly bound $A^2\Sigma^+$ state. Perhaps the most interesting numbers are the values for the $^{3}\Pi$ hyperfine parameters which have been assembled in Table 5. They clearly represent a marked improvement over the previous determination which was very much at the limit of the experimental method [8] despite the large size of the interaction. Of the four values, only those for $h_{\Pi}^{(2)}$ are in reasonably good agreement with the earlier work; this is because they are derived from LMR measurements on HF$^+$ in the $^3\Sigma^+$ level in both studies. The same remark might be expected for the values of $h_{\Pi}^{(1)}$ and $h_{\Pi}^{(3)}$.

To be expected to apply to the corresponding parameter for the $^2\Sigma^+$ ground state, $h_{\Sigma}^{(2)}$, but in this case the agreement is not so good. This possibly reflects the values to which our other hyperfine parameters were constrained in the fit. We have estimated the values by scaling those for the OH radical, a procedure which is only moderately vindicated by the value for $h_{\Sigma}^{(2)}$ determined via the values expected was 82.58 MHz. Hovde et al. [8] appear to have constrained these other parameters to zero. The first full determination of the $^{3}\Pi$ hyperfine parameters in HF$^+$ provides information about the distribution of the open-shell electrons in this molecule. The various experimental values [30] and their experimental determined values are given in Table 6. In this table, they are compared with the values calculated ab initio by Kristiansen and Veseth [13] and with the corresponding values calculated for the atomic ion F$^+$ [31].

It can be seen that the values of Kristiansen and Veseth are remarkably good (with the slight exception of the spin density at the $^2\Sigma^+$ nucleus which is notoriously difficult to calculate reliably). The expectation values for F$^+$ are also close to those for HF$^+$, consistent with a description of an open-shell electronic wavefunction that is confined largely to the F atom. In their experimental study of the line-structure spectrum of F$^+$, Brown et al. [15] suggest that the value for $\langle \delta \rangle$, should be raised to 0.170 (55) au, which would then be slightly larger than the value determined for HF$^+$. As can be seen in Table 3, we have been able to determine three of the possible six g-factors for a molecule in a $^3\Sigma^+$ state. The orbital g-factor $g_{2}^{o}$ deviates from unity because of relativistic and non-adiabatic corrections [32]. The former is typically about $-1.5 \times 10^{-3}$, from which the non-adiabatic correction, $\alpha_{D}$, is calculated to be 1.33 (23) $\times 10^{-3}$. The rotational g-factor, $g_{s}$, has nuclear and electronic contributions.

The nuclear contribution depends only on the nuclear masses and charges for a diatomic molecule [30]; for HF$^+$, it is calculated to be 0.5300 $\times 10^{-3}$ (in units of Bohr magnetons) leaving $g_{s}$ as 1.09 (13) $\times 10^{-3}$. The two parameters $\alpha_{D}$ and $g_{s}$ have essentially the same physical origin in the effective Hamiltonian, both depending on the admixture of $\Sigma$ and $\Delta$ states [32]. However, while $\alpha_{D}$ depends on the relative population of the lowest state of HF$^+$, $g_{s}$ depends on their sum. Thus if a $^3\Sigma^+$ state is dominated by $\Sigma$ states alone, $\alpha_{D}$ is equal to $g_{s}$. Our experimental result shows that this is the case, to within experimental error, and we thus have evidence that the $^3\Sigma^+$ state of HF$^+$ is dominated primarily by $\Sigma$ states. The other $g$-factor determined in our fit is $g_{2}^{o}$, the anisotropic correction to the electron spin magnetic moment. Though the value in Table 3 $0.90 (31) (10^{-3})$ is not very precisely determined, it agrees reasonably well with the expectations of Curie's relationship [33], $-\gamma_{e}^{2}$ or 0.085 $\times 10^{-3}$. However, it should be remembered that $\gamma_{e}$ is an effective parameter in our fit, containing a contribution from the parameter $\alpha_{D}$ also [24].
4. Discussion

Although the measurements of the far-infrared LMR spectrum of HF$^-$ in the $v = 0$ level of its $X^2\Sigma^+$ state are not very extensive, they have allowed the determination of an essentially complete set of molecular parameters in the effective Hamiltonian, including the $\tilde{H}_2^+$ hyperfine parameters. The values determined are also significantly more accurate than those obtained previously by optical spectroscopy [6] and by a combination of far-infrared LMR and infrared spectroscopy [8], as shown in Tables 4 and 5. Using our values for the ground state parameters and the value for $\gamma_0$ of $1.010\,600$ (32) A$^2$ where the quoted error is purely statistical. This equilibrium bond length is significantly longer than that of this ground of HF$^-$[0.9161(9)]. The lambda-doubling parameters are also much better determined, particularly the combination ($\delta + \gamma$) which governs the doubling in the $^2\Sigma^+$ component: the present study gives values for $\mu$ and $\gamma$ of 0.88 and 0.94 cm$^{-1}$, respectively. An important feature of their calculation was the inclusion of the effect of the continuum of vibrational levels above the weakly bound $^2\Pi$ state.

Perhaps the most interesting numbers are the values for the $^2\Pi$ hyperfine parameters which have been assembled in Table 5. Clearly they represent a marked improvement over the previous determination which was made at the limit of the experimental method [8] despite the large size of the interaction. Of the four values, only those for $\mu_\Pi(2)$ are in reasonably good agreement with the earlier work; this is because they are derived from LMR measurements on HF$^-$ in the $X^2\Sigma^+$ levels in both studies. The same remark might be extended to the study of the $^2\Pi$ state.

It can be seen that the values of Kristiansen and Vesten are remarkably good (with the slight exception of the spin density at the $^2\Pi$ nucleus which is notoriously difficult to calculate reliably). The expected values for $F^-$ are close to those for HF$^-$, consistent with a description of an open-shell electronic wavefunction which is confined largely to the F atom. In their experimental study of the fine-structure spectrum of $F^-$, Brown et al. [15] suggest that the value for $\delta_{HF}^-$ should be raised to 0.170 (55)$\alpha_U$, which would then be slightly larger than the value determined for HF$^-$.

As can be seen in Table 3, we have been able to determine three of the possible $g$-factors for a molecule in a $^2\Pi$ state. The orbital $g$-factors $g_\|$, determined from the $\mu$ values by relativistic and non-adiabatic corrections [32]. The former is typicallly about $-1.5 \times 10^{-6}$, from which the non-adiabatic correction, $\delta g_\|$, is calculated to be $1.33 (23) \times 10^{-5}$. The rotational $g$-factor $g_\tau$ has nuclear-electronic contributions.

$$ g_\| - g_\tau $$

The nuclear contribution depends only on the nuclear masses and charges for a diatomic molecule [30]; for HF$^-$, it is calculated to be $0.5300 \times 10^{-3}$ (in units of Bohr magnetons) leaving $g_\tau$ as $1.10 (13) \times 10^{-5}$. The two parameters $\mu_\Pi$ and $\gamma_\Pi$ have essentially the same physical origin in the effective Hamiltonian, both depending on the admixture of $\Sigma$ and $\Delta$ states [32]. However, $\delta g_\|$, depends on the electronic configuration of these two effects, $g_\|$, being more sensitive to the $^2\Pi$ state than the $^2\Sigma^+$ state. The values in Table 3 (0.39 (31) $10^{-5}$) are not very precisely determined, it agrees reasonably well with the expectations of Cuts's relationship [33], $g_\| \approx 0.865 \times 10^{-5}$. However, it should be remembered that $\gamma_\Pi$ is an effective parameter in our fit, containing a contribution from the parameter $\alpha_{HF}^-$ also [24].
We have used the values for the molecular parameters in Table 3 to calculate the zero-field rotational spectrum of HF. The computed values of the transition frequencies for levels up to J = 9/2 are given in Table 7.

For the sake of simplicity, the relatively small proton hyperfine splittings have not been included. The computed linestrengths S_{HF} and those also listed in Table 7, can be used to assess the relative intensities of individual transitions. The linestrength is defined by

\[ S_{HF} = \frac{(\langle F'|F\rangle}\langle 2J + 1\rangle \frac{1}{2}}{\text{where the quantity on the right-hand side is the reduced matrix element of the rotation matrix [34] and } \beta \text{ stands for subsidiary quantum numbers. The intensity of the line in absorption can be obtained by multiplying the linestrength by the square of the dipole moment } \mu, \text{ by the transition frequency } \nu \text{ and by the population difference between the lower and upper states. The Einstein } A \text{-coefficients for spontaneous emission from state } i \text{ to } j \text{ can also be calculated from the linestrengths by use of the relation } A_{ij} = (4\pi^4 \beta^2 \mu^2 \langle 2J + 1\rangle) S_{ij}.\]

Table 7 is not quite complete because the fine-structure transitions with \( \Delta J = 1 \) (R-lines) have been omitted. These transitions are very weak and occur at considerably higher frequencies (at wavelengths shorter than 2200 Å).

This paper describes a study of the far-infrared LMR spectrum of the HF radical which is incomplete. The work was curtailed prematurely by the unexpected illness and death of Ken Evenson in 2002. It was in fact the last piece of experimental work to be carried out in his laboratory at Boulder before it was closed down. Consequently, much remains to be done on this interesting molecule. Several other coincidences with short-wave laser lines await investigation. It might also be possible to study some transitions in the HCl molecule despite their slow natural linewidth because there is such a suitable laser lines very close in frequency. Finally, it could well be that HF** is sufficiently energized in the microwave discharge that it would be possible to study its spectrum in excited vibrational levels.

Acknowledgments

MDA is grateful for the support of a NRC Postdoctoral Fellowship. This study was supported in part by NASA contract W15.047.

References

Table 7
Calculated rotational and fine-structure transition frequencies of the HF* radical in the $\nu = 0$ level of the $\Delta \Sigma$ transition

<table>
<thead>
<tr>
<th>$\Delta \Sigma$</th>
<th>$\Delta \nu'$</th>
<th>$\nu'$</th>
<th>$F$</th>
<th>$F'$</th>
<th>$\nu$ (MHz)</th>
<th>Vacuum wavelength (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\Sigma^{-}$</td>
<td>0 - 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>290396 (4.6)</td>
<td>5717.62</td>
</tr>
<tr>
<td></td>
<td>1 - 2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>291690 (4.5)</td>
<td>5769.09</td>
</tr>
<tr>
<td></td>
<td>2 - 3</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>292994 (4.5)</td>
<td>5819.00</td>
</tr>
<tr>
<td></td>
<td>3 - 4</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>294297 (4.5)</td>
<td>5869.54</td>
</tr>
<tr>
<td></td>
<td>4 - 5</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>295599 (4.6)</td>
<td>5919.58</td>
</tr>
<tr>
<td></td>
<td>5 - 6</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>296902 (4.6)</td>
<td>5969.68</td>
</tr>
<tr>
<td>$^{1}\Sigma^{+}$</td>
<td>0 - 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>282263 (4.6)</td>
<td>5494.30</td>
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<tr>
<td></td>
<td>1 - 2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>283564 (4.6)</td>
<td>5533.01</td>
</tr>
<tr>
<td></td>
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<td>3</td>
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<td>5608.56</td>
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<td>4 - 5</td>
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<td>4</td>
<td>287462 (4.5)</td>
<td>5644.46</td>
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<tr>
<td></td>
<td>5 - 6</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>288760 (4.6)</td>
<td>5680.00</td>
</tr>
</tbody>
</table>

*Coupling scheme: $J = N + S + F_1 = F + F_2 + F_2$, where $F_1$ and $F_2$ are the $^3\Sigma^{-}$ and $^1\Sigma^{+}$ nuclear spin respectively. The proton hyperfine splittings are not included.

For definition, see Eq. (6).

*Estimated uncertainty in units of the last quoted decimal place (1σ).

*Transition not directly studied in the LMR experiment.

We have used the molecular values for the functional parameters in Table 1 to calculate the zero-field rotational spectrum of HF*. The computed values of the transition frequencies for levels up to $J = 9/2$ are given in Table 7.

For the sake of simplicity, the relatively small proton hyperfine splittings have not been included. The computed line strengths $S_{\nu J}$, which are also listed in Table 7, can be used to assess the relative intensities of individual transitions. The line strength is defined by

$$S_{\nu J} = \left| \langle F' | F | \nu \rangle \langle \alpha' | \alpha \rangle \right|^2,$$

where the quantity on the right-hand side is the reduced matrix element of the rotation matrix [34] and $\nu$ stands for subsidiary quantum numbers. The intensities of the line in absorption can be obtained by multiplying the line strength by the square of the dipole moment $\mu$, by the transition frequency and by the population difference between the upper and lower states. The Einstein $A$-coefficients for spontaneous emission from state $i \rightarrow j$ can also be calculated from the line strengths by use of the relation

$$A_{ij} = \sum_{\nu J} \frac{1}{2} S_{\nu J} \delta_{\nu J} \left(2F' + 1\right) S_{\nu J}.$$

Table 7 is not quite complete since the fine-structure transitions with $\Delta \Sigma = 1$ (R-lines) have been omitted. These transitions are very weak and occur at considerably higher frequencies (at wavelengths shorter than 25 Å).

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References

Millimeter-wave spectrum of BrCN produced by de discharge
Pradeep Risikrishna Varadwaj and A.I. Jaman*
Saha Institute of Nuclear Physics, IAF Balibagh, Kolkata 700064, India
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Abstract
Ground state (σ−0) and first excited state (σ+1) millimeter-wave rotational absorption spectra of cyanogen bromide (BrCN) and some of its isotopic species, have been investigated in the frequency region 40.0–75.0 GHz using a source-modulated millimeter-wave spectrometer. Millimeter-wave radiation has been produced using a frequency multiplier, the fundamental radiation source being klystrons. BrCN has been produced by applying a dc glow discharge through a mixture of 3-bromobenzonitrile and trifluoromethy bromide (CF3Br) at low pressure. The quadrupole hyperfine structure of 35Br and 37Br have been resolved, measured, and analyzed. Finally, intermolecular distances of BrCN have been determined.

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Keywords: Millimeter-wave spectroscopy; Cyanogen bromide (BrCN); Discharge; Molecular structure

1. Introduction
Production of molecules by dc glow discharge has proved to be a very important and useful technique. This technique appears to be highly suitable for the generation of transient species which are difficult to synthesize by ordinary chemical methods. Cyanogen fluoride FCN [1] and many halogen derivatives of acetylene compound HCCF [2], HCCCF [3], CIHCF [4], BrCF [5], FCCN [6], etc., have been produced by dc glow discharge and were characterized by various spectroscopic methods. However, the production of cyanogen bromide (BrCN) using dc glow discharge method has not yet been reported. Analysis of pure rotational transitions of BrCN (J = 2 → 3) was first reported by Townes et al. [7]. Subsequently, Burden and Townes [8] have analysed the quadrupole hyperfine structure of the Br nucleus. Later on, the J = 3 → 4 rotational transitions of BrCN have been observed and analyzed by Gordy et al. [9,10]. The rotational analysis has been extended to the millimeter-wave region by Burrus et al. [11] and to the millimeter-wave and sub-millimeter-wave region by Le Guennec et al. [12] who have reported only the quadrupole free line centers. The microwave spectra for J = 0 → 1 and J = 1 → 2 of BrCN have been reported by Cogley et al. [13]. Millimeter-wave spectra of 35NBr species of BrCN has been analysed by Tamassia et al. [14] in the ground and in some low-lying excited vibrational states. However, in all the previous works, BrCN was either produced commercially or prepared chemically.
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Analysis of the rotational spectra of C2CN produced by dc glow discharge is underway and will be reported in a separate communication.

* Corresponding author. Fax: +91-33-2317-4657.
Email address: jaman@enmp.saha.ernet.in (A.I. Jaman).
Millimeter-wave spectrum of BrCN produced by dc discharge
Pradeep Risrikishna Varadwaj and A.I. Jaman*
Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700 064, India
Received 22 October 2003; in revised form 7 May 2004
Available online 8 June 2004

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Analysis of the rotational spectrum of 13CN produced by dc glow discharge is underway and will be reported in a separate communication.

E-mail address: jaman@sfmp.saha.ernet.in (A.I. Jaman).

* Corresponding author. Fax: +91-33-2337-4037.

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Millimeter-wave spectrum of BrCN produced by dc discharge

Pradeep Rishtiksha Varadwaj and A.I. Jaman*
Saha Institute of Nuclear Physics, IAF Bidhannagar, Kolkata 700 064, India
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Analysis of the rotational spectrum of CICN produced by dc glow discharge is underway and will be reported in a separate communication.