Infrared Fourier Transform Emission Spectroscopy

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1 Introduction

Traditionally high-resolution infrared spectra of gas-phase molecules are recorded in absorption and the advantages of acquiring infrared emission spectra have largely been overlooked. As this article will illustrate, using mainly our own work, all else being equal, infrared emission spectroscopy is more sensitive than absorption spectroscopy. Since transient molecules have low concentrations because of their great chemical reactivity, it is advantageous to use emission spectroscopy to study them.

The infrared region of the electromagnetic spectrum provides a unique window for monitoring molecular processes. Mainly vibrational transitions of molecules are found in the infrared, although there are infrared electronic transitions and infrared pure rotation transitions. In general, vibrational transitions carry specific chemical group information in a way that electronic and pure rotational transitions do not. It is for a good reason that the organic chemist refers to the 900—1400 cm^{-1} interval as the 'fingerprint region'.

All molecules, except homonuclear diatomics, have at least one electric-dipole-allowed vibrational transition. Even homonuclear molecules such as H_2 have weak electric-quadrupole transitions which are used by astronomers to detect molecular clouds that are experiencing shock waves.[1] Vibrational transitions are thus a universal, molecule-specific monitor of chemical composition; every major industrial laboratory and university chemistry department has at least one infrared spectrometer.

Vibrational spectroscopy also has some deficiencies. Perhaps the most intrinsic problem is that vibrational transitions are relatively weak. A 'typical' molecule such as CH has a dipole moment of 1.43 Debye, a transition dipole moment of 0.134 Debye for the fundamental $v=1 \leftarrow 0$ vibrational transition and a transition dipole moment of 0.70 Debye for the $A^2\Delta$–$X^2\Pi$ electronic transition.[2,3] Since the relative intensity depends on the square of the transition dipole moment, the vibrational transition is about 100 times weaker than the pure rotational or the electronic transition. For the spectroscopy of stable molecules, this intrinsic weakness is hardly a problem – one simply uses a little more sample. For the infrared vibrational spectroscopy of transient molecules at low concentrations, this relative lack of sensitivity puts the technique at a serious disadvantage. Emission spectroscopy is one technique that improves the infrared performance of a spectrometer.

The infrared region of the electromagnetic spectrum suffers from some other technical deficiencies. For example there is no infrared equivalent of the visible dye laser or the microwave klystron that provides widely tunable radiation. On the horizon are infrared optical parametric oscillators (OPOs) which will provide tunable, single-mode, high-power radiation.[4]

Infrared detectors and infrared materials such as windows and lenses also tend to be inferior and more expensive that the corresponding visible components. The infrared analogue of the photomultiplier tube for the measurement of low radiation levels is not available. Recently, however, a solid state Si: As avalanche infrared detector has been manufactured by Rockwell.[5]

For the visible and ultraviolet region, it is well-known that emission spectroscopy is more sensitive than absorption spectroscopy because emission spectra have 'zero background.' In an ideal absorption experiment, the noise arises mainly from shot-noise from the background continuum. By comparison, in an emission experiment, the noise is reduced because the continuum is absent. Of course the total signal level is also reduced in an emission experiment compared to an absorption experiment but the overall signal-to-noise ratio is increased because the noise has declined much more than the signal. For example the violet colour often seen in a flame is due to the easily detected $A^2\Delta \rightarrow X^2\Pi$ emission of the CH molecule. The detection of the corresponding absorption due to the CH molecule in a flame is possible but constitutes a much more difficult experiment.[6]

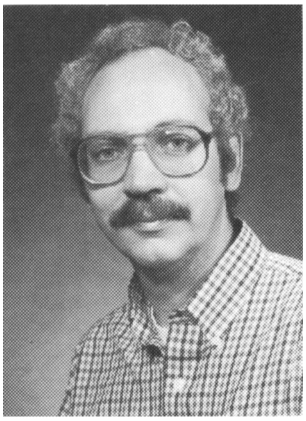
What is surprising to many people is that the advantages of emission spectroscopy persist into the infrared. Infrared spectrometers are routinely operated in absorption, not emission. Infrared emission spectroscopy requires that the sample be at a different temperature (higher or lower) than the spectrometer. Higher temperatures are more favourable since the emitted power increases strongly with temperature. Infrared emission spectroscopy is plagued by thermal blackbody emission from the spectrometer itself as well as from the furnace or electrical discharge used to heat the sample. This blackbody emission is a continuum that provides nothing but noise. The Planck function is a law of nature that can never be entirely avoided in the infrared. By limiting the field of view with cold apertures and by good optical design (*e.g.* by avoiding having the spectrometer look directly at a hot surface), as well as by limiting the spectral range of the detectors with cold filters, the effects of unwanted blackbody emission can be minimized.

Another apparent difficulty is that the rates of emission are much smaller in the infrared than in the visible or ultraviolet. For example, the violet $A^2\Delta \rightarrow X^2\Pi$ transition of CH has a radiative lifetime[3] of 526 ns or an Einstein *A* value (reciprocal of the lifetime) of 1.9×10^6 s^{-1}. This compares to a vibrational lifetime of 8.7 ms or an Einstein *A* value of 115 s^{-1} for the $v=1 \rightarrow 0$ transition.[2] Since the Einstein *A* value is the rate per molecule of photon emission, the emission rates are obviously much smaller for vibrational transitions than for electronic transitions. This is due to both the ν^3 term in the formula[7] in eqn. (1):

$$A=\frac{16\pi^3\nu^3}{3\epsilon_0 hc^3}|\mu|^2 \qquad (1)$$

for the Einstein *A* factor and the relative weakness of vibrational transitions. Nevertheless the infrared emission rates are adequate to provide an acceptable signal-to-noise ratio for CH[8] (Fig. 1) or even for a transient molecule such as LiH in the far-infrared region[9] (Fig. 2).

We discovered the power of infrared emission spectroscopy by serendipity. At the request of the astronomer J. Keady we were trying to record an absorption spectrum of SiS[10] at 750 cm^{-1} (Fig. 3) to match molecular features in an infrared spectrum of a carbon



Peter Bernath was born in 1953 in Ottawa, Ontario, Canada. Following his B.Sc. degree from the University of Waterloo (1976), he received a PhD in physical chemistry from MIT in 1980. After a post-doctoral stint at the National Research Council of Canada, he became a faculty member at the University of Arizona from 1982–1990. In 1991 he took up his present position as Professor of Chemistry & Physics at the University of Waterloo, while maintaining a connection with the University of Arizona.

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star The experimental plan was simple heat Si powder and SiS_2 solid to 1000 °C to make SiS by the reaction (2)

$$Si(s)+SiS_2(s)\rightarrow 2SiS(g) \tag{2}$$

The hot molecules would then be detected by absorption of infrared light from a glower Much to our amazement a very high quality emission spectrum was recorded in only 14 minutes of data collection[10] (Fig 4)

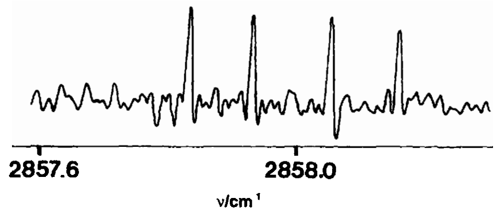

Figure 1 The CH R(4) vibration–rotation emission line for the $v=1\rightarrow0$ transition of the $X^2\Pi$ state The quartet pattern is characteristic of a $^2\Pi$ state that follows Hund s case (*b*) coupling

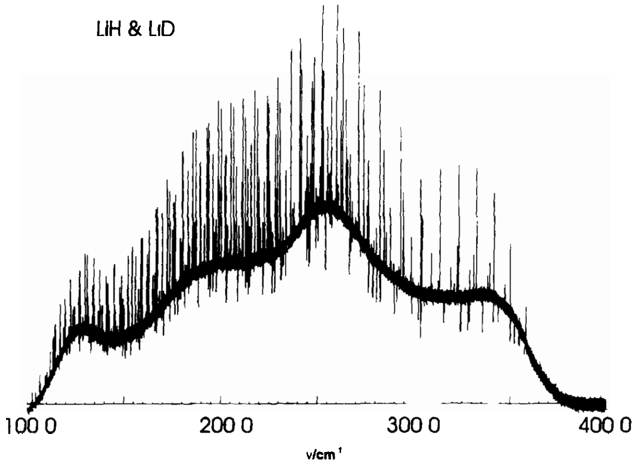

Figure 2 The far infrared pure rotational emission spectrum of LiH and LiD in the 100–400 cm $^{-1}$ region The absorption features are due to water vapour impurity

In 1989 when our SiS experiments were carried out with the McMath Pierce Fourier transform spectrometer of the National Solar Observatory in Tucson, Arizona, there were scarcely any published examples of high resolution emission spectra at long wavelengths Apart from a relatively low resolution spectrum of GeS [11] only the infrared emission spectrum of the FO[12] molecule was available in the literature The FO molecule was produced by the very exothermic reaction (3)

$$F+O_3\rightarrow FO+O_2 \tag{3}$$

and for some time we were convinced that an energetic reaction was necessary to see emission Soon we recorded the thermal emission spectrum of BeF_2 (Fig 5), proving that no chemical reactions are necessary to provide additional vibrational excitation [13]

Thermal emission spectra are, in fact, used to monitor atmospheric molecules such as O_3 in the stratosphere both from balloon platforms[14] and satellites [15] Thin films of solids and liquids also give excellent thermal emission spectra[16] (Fig 6) Of course, spectra of materials in condensed phases are at low resolution

2 Infrared Electronic Transitions

Most people find the idea of infrared electronic transition to be almost a contradiction, since most stable molecules typically have electronic transitions in the ultraviolet region Many transient molecules such as ions or free radicals, however, have visible or infrared electronic transitions because of the presence of unpaired electrons in low lying orbitals While these reactive molecules cannot be purchased from a chemical supply company they are, in fact very common In energetic environments such as in flames, explosions, upper atmosphere stellar atmospheres and the interstellar medium, transient molecules are abundant and dominate the chemistry

Transient molecules can be made in the laboratory by the application of electrical discharges, heat or light to stable precursor

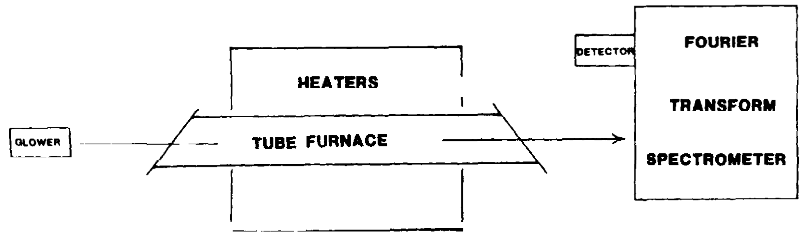

Figure 3 The experimental arrangement for high temperature emission and absorption spectroscopy For absorption spectroscopy the glower is turned on to provide a source of continuum radiation while for emission spectroscopy the glower is turned off Note that both emission and absorption experiments use the emission port of the Fourier transform spectrometer

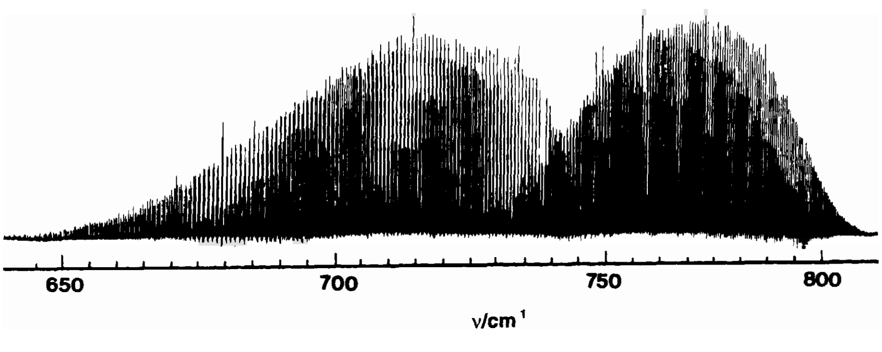

Figure 4 Vibration–rotation emission spectrum of the SiS molecule near 13 μm (650–800 cm $^{-1}$) Notice the P branches 740–800 cm $^{-1}$ and the R branches 650–740 cm $^{-1}$ of the $1\rightarrow0$ $2\rightarrow1$ $3\rightarrow2$ *etc* vibrational bands

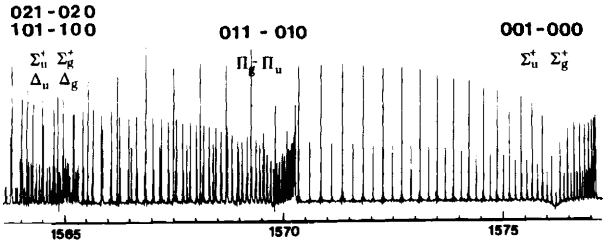

Figure 5 The vibration–rotation emission spectrum of the $\nu_3(\sigma_u)$ mode (antisymmetric stretching vibration) of the linear BeF$_2$ molecule The R branch band head of the ν_3 fundamental is on the right edge of the figure In the middle is the head for the first bending hot band 011—010 and to the left of the figure are two heads associated with other hot bands

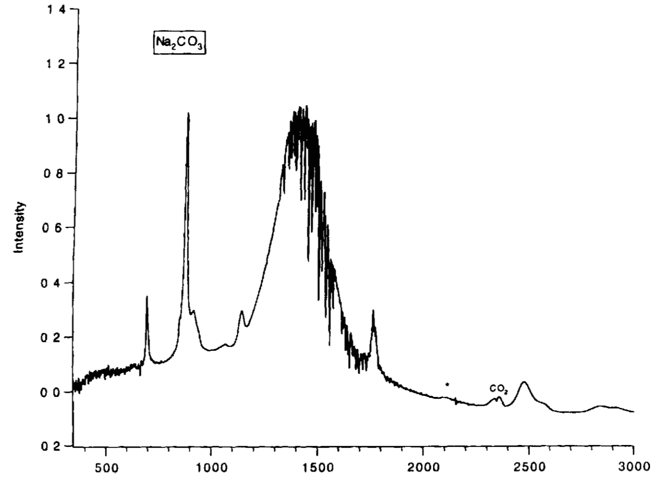

Figure 6 Emission spectrum of a thin film (100–200 μm thick) of solid Na$_2$CO$_3$ at a temperature of about 400 °C The two peaks marked with asterisks are due to Na$_2$SO$_4$ impurity The effect of water absorption near 1500 cm^{-1} and CO$_2$ emission near 2300 cm^{-1} can be seen in the spectrum

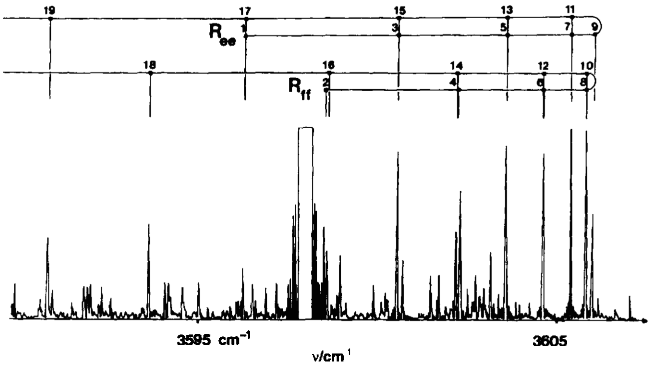

Figure 7 The 0–0 band of the B$^1\Delta_g$→A$^1\Pi_u$ electronic transition of the C$_2$ molecule Notice the band heads in the two R branches near 3605 cm^{-1}

molecules For example the microwave discharge (2 45 GHz) of the hydrocarbons allene (CH$_2$=C=CH$_2$) or methane (CH$_4$) resulted in the production of the C$_2$ molecule [17] The new B$^1\Delta_g$–A$^1\Pi_u$ infrared electronic transition[17] was observed in emission near 3600 cm^{-1} (Fig 7) Since the visible Swan system of C$_2$ (d$^3\Pi_g$→a$^3\Pi_u$) and the near infrared Phillips system (A$^1\Pi_u$→X$^{1+}\Sigma_g$) are readily detected in flames and in comets,[18] the new infrared B$^1\Delta_g$→A$^1\Pi_u$ transition should also be present

Infrared electronic transitions of polyatomic molecules are also well known, for example, for C$_3$[19] and HO$_2$ [20] A pioneering high resolution emission spectrum of the HO$_2$free radical was recorded with a SISAM spectrometer near 7000 cm^{-1} (1 45 μm) [20] The HO$_2$ molecule is a key trace constituent of the earth's atmosphere [14]

Infrared electronic transitions are particularly important for systems which contain transition elements Molecules with transition metals typically have a large number of low-lying electronic states and many unpaired electrons This means that the visible and ultraviolet electronic transitions are very complex because of the high density of states and the resulting perturbations In the infrared region the energies of the states are lower and the density of states is correspondingly reduced The infrared electronic transition of a molecule such as YN[21] (Fig 8) is thus particularly simple and unperturbed The YN molecule was made by sputtering Y metal in a hollow cathode with Ne gas in the presence of a trace of N$_2$

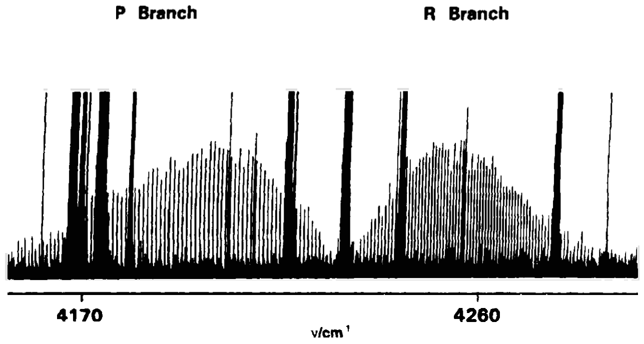

Figure 8 The 1–1 vibrational band of the A$^1\Sigma^+$→X$^1\Sigma^+$ electronic transition of the YN molecule Since the rotational constants are very similar in the A$^1\Sigma^+$ state and in the ground X$^1\Sigma^+$ state, there is no bandhead

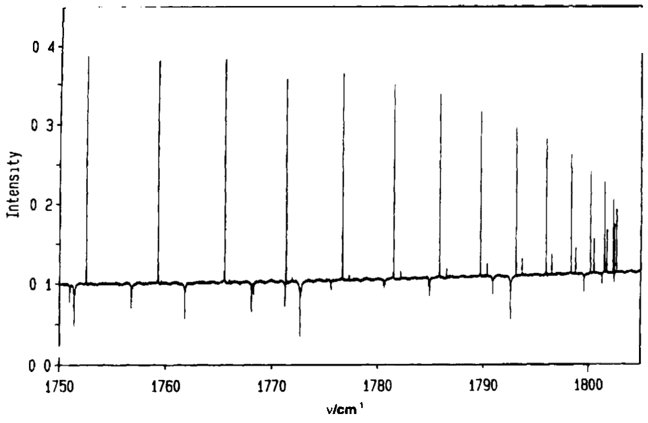

Figure 9 The vibration–rotation emission spectrum of the R branch of the fundamental 1→0 vibrational band of AlH The high temperature (1550 °C) makes it possible to see the R branch bandhead near 1800 cm^{-1} at R(26) The absorption features are due to the impurity H$_2$O, both in the spectrometer (sharp absorptions) and in the short path of laboratory air between the furnace and the spectrometer (wider absorptions)

3 Infrared Vibration–Rotation Transitions

Vibration-rotation emission spectroscopy above 1800 cm^{-1} is not rare, even for transient molecules such as CH[8] (Fig 1) This magic number of 1800 cm^{-1} (5 5 μm) is the band gap of the InSb detector The InSb detector has nearly unit quantum efficiency and is the best infrared detector but it does not work for wavenumbers below 1800 cm^{-1} The detection of emission at longer wavelengths is thus more difficult but excellent spectra can be recorded (Fig 4) In Fig 9 the emission due to AlH molecules was recorded at a resolution of 0 005 cm^{-1} with a signal-to-noise ratio of more than 150 for the strong lines [22] The measurement precision of 0 0002 cm^{-1} (6 MHz) is remarkable for a transient molecule

Emission spectroscopy will work at even longer wavelengths as illustrated with the SiS spectrum[10] (Fig 4) Even in the far infrared region it proved possible to record the vibration–rotation emission

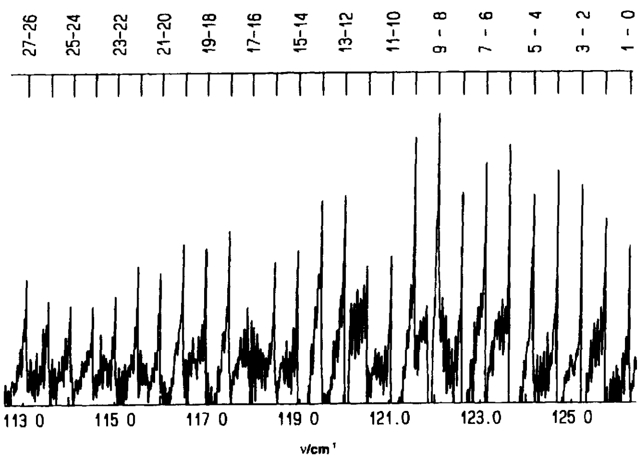

Figure 10 The vibration–rotation emission bands of CsI near 100 cm^{-1}. No individual rotational lines could be resolved but the 1→0 to 27→26 vibrational bandheads are marked in the spectrum.

spectrum of CsI[23] near 100 cm^{-1} (Fig. 10). In this case the individual rotational lines were not resolved because the rotational constant, B, has a value of 0.02 cm^{-1}. Nevertheless the 1–0 to 30–29 bandheads could be measured. The observation of vibration–rotation bandheads is rare in room-temperature spectra but they are a common feature of high temperature spectra (Figs. 5, 9 and 10).

Vibration–rotation emission spectra are also readily recorded for polyatomic molecules such as BeF_2 (Fig. 5) and C_{60} (Fig. 11). The linear BeF_2 molecule is isoelectronic with CO_2 and the rotational structure was analysed to give an equilibrium Be–F bond length of 1.37297 Å.[13] For C_{60} the rotational lines were not resolved (Fig. 11) but the band positions could be tracked as a function of temperature to determine an extrapolated 0 K band centre.[24] The gas-phase positions of the C_{60} bands at low temperature were used in a search for C_{60} in carbon-rich stars.[25]

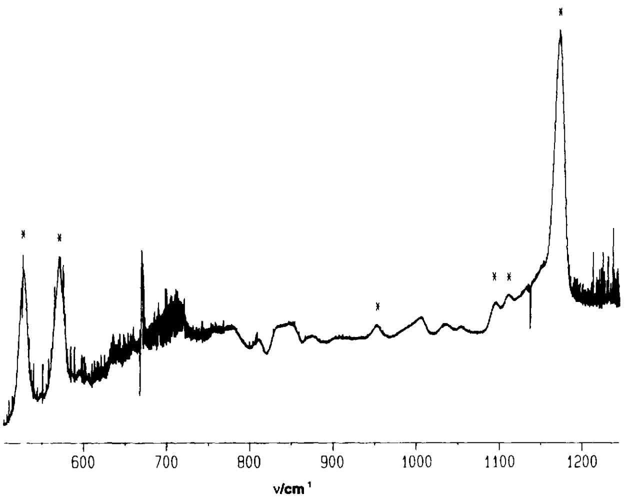

Figure 11 The vibration–rotation emission spectrum of gaseous C_{60}. The C_{60} bands are marked with asterisks. The sharp features between 500 and 900 cm^{-1}, and above 1150 cm^{-1} are due to emission from hot water and carbon dioxide impurities.

4 Pure Rotational Emission Spectra

Small gas-phase molecules with large rotational constants have pure rotational spectra in the far-infrared and infrared regions. The emission spectrum of the transient molecules LiH and LiD[9] (Fig. 2) was recorded in the far-infrared region to show feasability and to explore the effects of the breakdown of the Born–Oppenheimer approximation.

One application of pure rotational emission spectroscopy was the detection of water vapour on the sun.[26] An infrared spectrum of a sunspot (Fig. 12) was recorded with the McMath-Pierce Fourier transform spectrometer at Kitt Peak. A high density of absorption lines was found and they could not be assigned to a known spectrum of a molecule. We suspected that the mystery molecule was hot water at the sunspot temperature of 2900 °C. The pure rotational emission spectrum of water vapour at 1550 °C was recorded in the

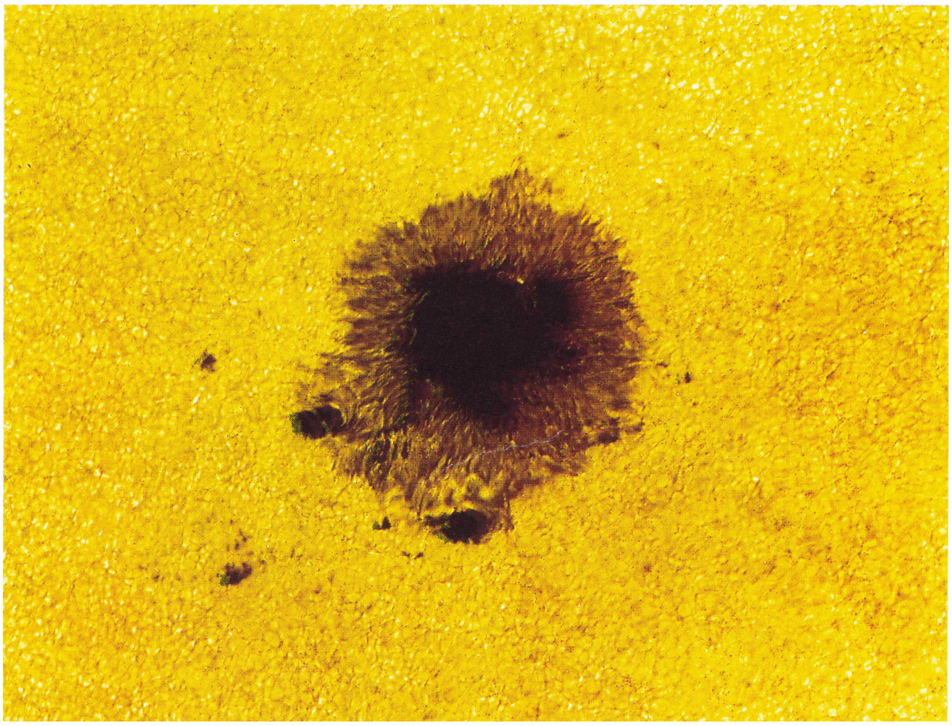

Figure 12 White light image of a sunspot (black) and the surrounding photosphere of the sun. The sunspot shows a dark, cool umbra (2900 °C) and a surrounding warmer penumbra. The photosphere of the sun shows granulation caused by the formation of convective cells on the surface of the sun.

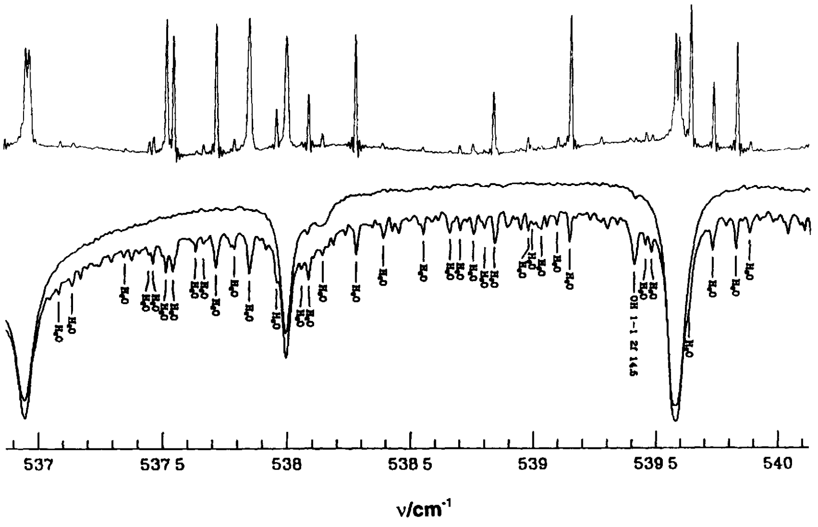

Figure 13 The upper panel is a portion of the pure rotational emission spectrum of hot water (1550 °C) recorded in the laboratory The lower panel has two traces of the solar spectrum The upper trace is a portion of the absorption spectrum of the penumbra of the sunspot showing only absorption features caused by water in the earth's atmosphere The lower trace is the spectrum of a sunspot showing additional absorption features due to hot water vapour (2900 °C) on the surface of the sun One pure rotation transition of the OH molecule can be seen near 539 4 cm^{-1}

laboratory in the 400–1000 cm^{-1} region The match between the line positions of the emission laboratory spectrum and the sunspot absorption spectrum was very good (Fig 13), identifying water on the sun[26]

5 Future Prognosis

The improvement in sensitivity obtained by working in emission rather than in absorption with high-temperature molecules, ions and free radicals is typically a factor of 10 in the mid-infrared region At the moment, the instrument of choice is the high-resolution Fourier transform spectrometer For astronomical applications for which the light levels are very low, the Fourier transform spectrometer is inferior in sensitivity to the cryogenic echelle spectrograph[27]

A cryogenic echelle spectrograph is a compact spectrometer that uses an echelle grating in high orders to obtain high resolution spectra The entire instrument is cooled to 77 K with liquid nitrogen to eliminate most of the background thermal emission from the spectrometer itself The infrared radiation is measured with a large format (512×512) array of InSb detectors Many of these spectrometers are under construction or have already been built at observatories around the world The anticipated performance for an instrument called Phoenix under construction at Kitt Peak National Observatory is spectacular[27] Phoenix will have a resolving power in excess of 100 000 at 2000 cm^{-1} (a resolution of 0 02 cm^{-1}) with a sensitivity 100 times higher than that of a Fourier transform spectrometer This quantum leap in performance promises to revolutionize both infrared astronomy and laboratory emission spectroscopy

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6 References

1 N Z Scoville, D N B Hall, S G Kleinmann and S T Ridgway, *Astrophys J* , 1982, **253**, 136
2 P F Bernath, *Annu Rev Phys Chem* , 1990, **41**, 91
3 W Bauer, B Engelhardt, P Wiesen and K H Becker, *Chem Phys Lett* , 1989, **158**, 321
4 For example, the entire November issue of *J Opt Soc Am B* , 1993, **10**
5 M D Petroff, M G Stapelbroek and W A Kleinhans, *Appl Phys Lett* , 1985, **51**, 406
6 L Lynds and B A Woody, *Appl Optics*, 1988, **27**, 1225
7 P F Bernath, *Spectra of Atoms and Molecules*, Oxford Univesity Press, New York, 1995, ch 1
8 P F Bernath, *J Chem Phys* , 1987, **86**, 4838
9 B Guo, K Q Zhang, M Dulick and P F Bernath, in preparation
10 C I Frum, R Engleman and P F Bernath, *J Chem Phys* , 1990, **93**, 5457
11 H Uehara, K Horiai, K Sueoka and K Nakagawa, *Chem Phys Lett* , 1989, **161**, 149
12 P D Hammer, A Sinha, J B Burkholder and C J Howard, *J Mol Spectrosc* , 1988, **129**, 99
13 C I Frum, R Engleman and P F Bernath, *J Chem Phys* , 1991, **95**, 1435
14 B Carli and M Carlotti, in *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*, ed K N Rao and A Weber, Academic Press, San Diego, 1992, 1
15 A E Roche, J B Kumer, J L Mergenthaler, G A Fly, W G Uplinger, J F Potter, T C James and L W Sterritt, *J Geophys Res* , 1993, **98**, 10763
16 P F Bernath *et al* , in preparation
17 M Douay, R Nietmann and P F Bernath, *J Mol Spectrosc* , 1988, **131**, 261
18 M F A'Hearn and M C Festou in *Physics and Chemistry of Comets*, ed W F Huebner, Springer Verlag, Berlin, 1990, p 101
19 H Sasada, T Amano, C Jarman and P F Bernath, *J Chem Phys* , 1991, **94**, 2401
20 R P Tuckett, P A Freedman and W J Jones, *Mol Phys* , 1979, **37**, 379
21 R S Ram and P F Bernath, *J Mol Spectrosc* , 1994, **165**, 97
22 J B White, M Dulick and P F Bernath, *J Chem Phys* , 1993, **99**, 8371
23 V Braun, B Guo, K Q Zhang, M Dulick, P F Bernath and G A McRae, *Chem Phys Lett* , 1994, **228**, 633
24 L Nemes, R S Ram, P F Bernath, F A Tinker, M C Zumwalt, L D Lamb and D R Huffman, *Chem Phys Lett* , 1994, **218**, 295
25 G C Clayton, D M Kelly, J H Lacy, I R Little Marenin, P A Feldman and P F Bernath, *Astronom J* , 1995, **109**, 2096
26 L Wallace, P Bernath, W Livingston, K Hinkle, J Busler, B Guo and K Q Zhang, *Science*, 1995, **268**, 1155
27 S T Ridgway and K H Hinkle, in *High Resolution Spectroscopy with the VLT*, ed M H Ulrich, ESO Conference and Workshop Proceedings, No 40, ESO, Garching bei Munchen, 1993, p 213