PART 6

THE INFRARED SPECTRUM

ATOMIC SPECTROSCOPY IN THE INFRARED*

E. BIÉMONT

Institut d'Astrophysique, Université de Liège, B-4000 Liège, Belgium

Abstract. Some recent developments of atomic spectroscopy in the infrared spectral range are briefly summarized. Different topics of interest for astrophysics, such as term analysis, far infrared measurements, isotope shifts, hyperfine structure observations and transition probability determination, are briefly considered.

Key words: atomic data – atomic processes – infrared: stars – line: identification

1. Introduction and Historical Comments

The interest of atomic spectroscopy for infrared solar physics can best be illustrated by a comparison of high resolution laboratory spectra obtained by Fourier Transform Spectroscopy (FTS) with recent recordings of the solar photospheric spectrum. As a specific example, Figure 1 shows that many infrared lines of the solar spectrum (Delbouille *et al.*, 1982) can easily be identified from a visual comparison with laboratory iron spectra (Biémont *et al.*, 1985a). In fact, the increasing resolution and signal-to-noise ratio which are now achieved for solar observations, and the possibility of disentangling the telluric and solar contributions (see *e.g.*, Farmer and Norton, 1989; Livingston and Wallace, 1991) require an increasing number of high quality atomic and molecular data.

Since the publication by Outred in 1978 of an extensive list of infrared lines (8885 lines belonging to 57 elements in the spectral range 1–4 μm), which was essentially a summary of the photographic and lead-sulfide observations available at that time, considerable progress has been made in infrared spectroscopy thanks to the use of FTS combined with improved detectors and more powerful computers. Further advances are also due to the use of more elaborate theoretical methods for investigating complex spectra and to the use of laser techniques in the far infrared region (Rydberg states spectroscopy and far-infrared laser magnetic resonance measurements).

The combination of FTS and hollow cathode (pulsed or not) has appeared to be very efficient not only for term analysis of neutral and singly ionized elements of solar interest but also for branching-ratio measurements, for isotope shifts, and hyperfine structure investigations.

2. Term Analysis

A recent summary has been published by Martin (1991). Due to space limitations, the references quoted in this section are restricted to neutral and singly ionized elements observed recently (in most cases after 1985) in the infrared region.

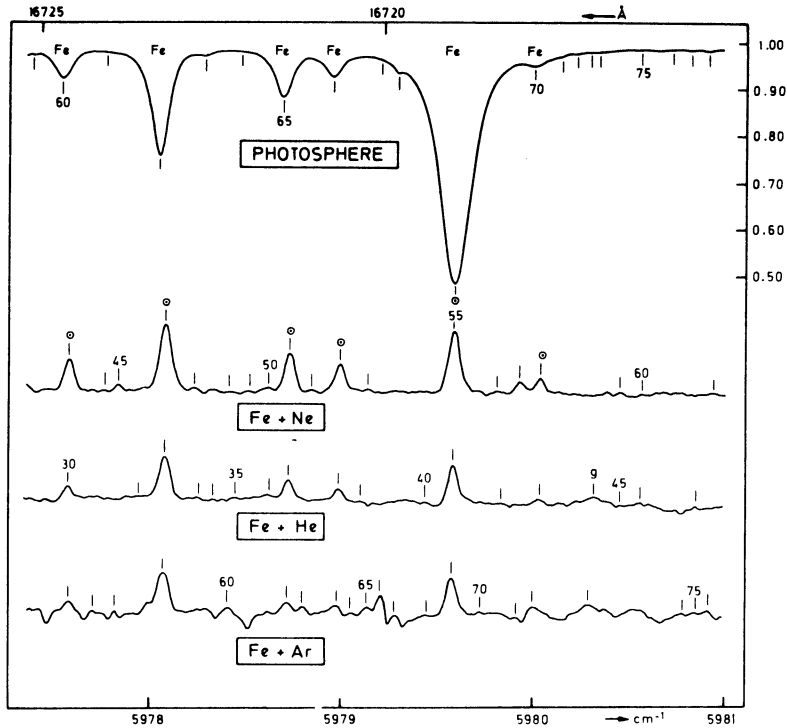* Dedicated to the memory of Prof. M. Migeotte (Liège University), who died on February 25, 1992.

Fig. 1. A comparison of the photospheric absorption spectrum (top) (Delbouille *et al.*, 1982) and of the FTS emission hollow-cathode spectra of iron (bottom) (Biémont *et al.*, 1985*a*)

2.1. THE LIGHT ELEMENTS ($Z = 1\text{--}19$)

The compilations published by NIST during the past 7 years concern He I (Martin, 1987), Mg I–XII (Kaufman and Martin, 1991*a*), Al I–XIII (Kaufman and Martin, 1991*b*), P I–XV (Martin *et al.*, 1985), S I–XVI (Martin *et al.*, 1990) and K I–XIX (Sugar and Corliss, 1985). New observations of magnesium (Mg I, II) and aluminum spectra (Al I, II) have been performed in the infrared region (1.1–5.5 μm) by Biémont and Brault (1986, 1987) using a hollow-cathode source and the 1m FTS of the National Solar Observatory (Kitt Peak). An analysis of the O II spectrum in the photographic region has been carried out recently by Wenker (1990). The non-penetrating states of O I have been considered by Chang *et al.* (1988) and infrared laser absorption spectra of Rydberg transitions of the same ion have been reported by Brown *et al.* (1987).

2.2. The Iron Group Elements $(21 \leq Z \leq 28)$

Sugar and Corliss (1985) have summarized the energy level data for the elements K through Ni ($Z = 19$–28). In addition, updated line or level lists have been published for different ions [Fe I–XXVI : Wiese (1985); Sc I–XXI : Kaufman and Sugar (1988); Ti I–XXI, Cr I–XXIV, Ni I–XXVIII : Wiese and Musgrove, (1989)]. Recent review papers are due to Johansson and Cowley (1988) and Johansson (1991).

Infrared FTS observations of Sc I were carried out by Ben Ahmed and Vergès (1977) (up to 3.39 μm) and the theoretical analysis is due to Ben Ahmed (1977). The analysis of Sc II was extended by Johansson and Litzén (1980) (0.11–1 μm). The Ti I spectrum has been recently reconsidered by Forsberg (1991) in the region 0.19–5.5 μm using the Kitt Peak FT spectrometer. The analysis of Ti II was extended in the infrared (up to 1.1 μm) by Huldt *et al.* (1982). Infrared observations of V I (1.0–5.6 μm) were due to Davis *et al.* (1978). A monograph by Iglesias *et al.* (1988) includes all the data available for V II (visible and near infrared regions). New FTS observations of V I and V II in the infrared region (1.1–5.5 μm) have been obtained by J. Brault at the NSO. The spectra, obtained with a hollow-cathode and three different carrier gases (He, Ne and Ar), are presently being analyzed by E. Biémont (Liège) and P. Quinet (Mons).

The Cr I and II FTS infrared observations in the range 1.1–5.5 μm reported by Biémont *et al.* (1985b) extended the range of the available observations. Solar identifications only were considered by these authors but the analysis of the Cr I term system has been undertaken at Imperial College, London. For Cr II, the NIST compilation was based upon results obtained by Johansson (1983) from observations extending up to 5 μm. Since the publication of the NIST compilation (Sugar and Corliss, 1985), the spectrum of Mn I has been investigated by Taklif (1990a) in the region 0.82–1.97 μm using an electrodeless discharge tube.

The iron spectrum has been the subject of infrared observations (1–4 μm) by Litzén and Vergès (1976), and the term system has been extended by Litzén (1976). New FTS high resolution infrared observations have been reported by Biémont *et al.* (1985a) who prepared an extensive table of solar identifications. The term analysis of these observations is being carried out by Learner at ICL. A table of 360 Fe I infrared lines has been published by Johansson and Learner (1990). More recently, the $3d^6$ (^5D)$5g$ subconfiguration of Fe II has been established (0.9–1.1 μm) (Rosberg and Johansson, 1992). They complement earlier observations in the near infrared by Johansson (1978) using a pulsed hollow-cathode discharge.

The only infrared observations of Co I used in the NIST compilation are due to Russell *et al.* (1940) and do not extend further than 1.1895 μm. FTS spectra of Ni I and II registered at Kitt Peak have led to many new solar identifications (Biémont *et al.*, 1986). The term analysis of Ni I is being carried out by Litzén (1992) and will be published soon. Approximately 625 lines have been identified in the region 1–5.5 μm. The most important new configurations involved in the observations are $3d^9 4f$, $5f$ and $5g$. Infrared observations of Ni II (1.8 μm) have been reported by Brault and Litzén (1983).

2.3. THE HEAVY ELEMENTS ($Z > 28$)

Several new compilations concerning all known spectra of Cu, Ge, Kr and Mo have
been published (Sugar and Musgrove, 1990, 1992, 1991 and 1988). The analysis
of Ga II has been extended by Isberg and Litzén (1985). Hollow-cathode spectra
of yttrium have been registered in the wavelength range 0.1–4.8 μm and a new
analysis of the Y II spectrum has been completed (Nilsson *et al.*, 1991). Sb I has
been the subject of two recent investigations in the lead-sulfide region by Hassini *et
al.* (1988) (0.25–2.48 μm) and by George and Azhar (1990) (1.0–3.0 μm). The In I
spectrum has been analyzed in the infrared by means of the FTS of the Laboratoire
Aimé Cotton, Orsay (France) (George *et al.* 1990). Since the publication of the
NBS tables for the lanthanides (Martin *et al.*, 1978), results have been reported for
Pr I (Ginibre, 1981), Pr II (Ginibre, 1989*a*,*b*, 1990), Nd II (Blaise *et al.*, 1984), Eu I
(Wyart, 1985) and Yb I (Aymar *et al.*, 1984). New observations have been published
for Pt I (Engleman, 1985; Reader *et al.*, 1990) and Pt II (Reader *et al.*, 1988, 1990).
Results have also been reported for Bi I (George *et al.*, 1985). A compilation of the
actinides has been prepared by Blaise and Wyart (1992).

3. Wavelength Standards in the Infrared

Compilations of reference wavelengths in the spectral range 15 to 25000 Å, have
been proposed by Kaufman and Edlén (1974) (the uncertainties lie between 0.0001
and 0.002 Å) and by Outred (1978). The new FTS measurements performed by
Engleman (1985) for Pt I do not extend to wavelengths longer than 0.722 μm and
the Pt II line list (Reader *et al.*, 1988) contains only 3 infrared lines above 1 μm.
A great deal of effort has been devoted to the production of standards for iron. An
extensive, older, list (4000 lines) produced by Crosswhite (1975) covered the spectral
range from 0.19 to 0.9 μm. The wavelength calibration of FTS Fe I emission spectra
has been discussed in detail by Learner and Thorne (1988). They have shown that
the accuracy of the calibration is limited by pressure shifts, by the inadequacy of
available standards and by effects of illumination. The only line list available for
the infrared region is due to Johansson and Learner (1990) (1.4–2.1 μm).

    The classical reference for calibrating wavelengths in the infrared region remains
the work of Norlén (1973) who reported accurate measurements for Ar I and Ar II
using a Fabry-Perot interferometer in the vacuum; 76 Ar I reference lines ($4p$–$3d$
and $4p$–$5s$ transitions) cover the photoelectric region up to 2.4 μm. As underlined
by Learner and Thorne (1988) from a comparison of their wavenumbers (Ar II)
with those of Norlén (1973), pressure shifts have to be considered with care when
calibrating the observed spectra. As the mean level shift in their work ($P = 3$ Torr)
is found, when compared to Norlén's measurements ($P = 0.2$ Torr), to increase
rapidly with the upper energy of the levels, the only lines suitable for calibration
are those involving low excitation levels.

4. Far Infrared Measurements

The spectroscopy of atoms in the far infrared region (FIR) (*i.e.*, roughly between
30 μm and 1 μm) is important because astrophysically abundant atoms (C, N, O,

Mg, Si, ...) or their isotopes can absorb or emit fine structure transitions in that region. The lines emitted can be used, for example, for the detection of atomic species in the cold interstellar medium or for the investigation of stratospheric composition. In fact atomic species such as C, O or Si can be studied very accurately only by far infrared (FIR) spectroscopy because their electronic transitions are not easily accessible to laser sources in the optical region.

FIR spectroscopy has seen a renewal during the past few years due to the development of new optically-pumped lasers [using CH_3OH, CH_2F_2 (*etc.*) molecules or their isotopes] and of liquid-helium-cooled bolometric detectors. A review paper on the subject has been published by Inguscio (1988). The FIR Laser Magnetic Resonance (LMR) technique is a sensitive, high resolution laboratory technique using an optically pumped laser as a source. The atoms to be investigated are situated inside the cavity of an optically pumped molecular laser. A change in the laser output is detected when a transition of the atom is tuned into coincidence with the laser transition by using an external magnetic field. The high sensitivity of the FIR-LMR technique has allowed spectroscopy of atomic fine structures, though it requires a close coincidence between an atomic transition and a known cw laser line and also the observation of M1 transitions (much weaker than the usual E1 transitions). The main fine-structure measurements obtained with that technique are summarized in Table 1. They appear considerably more accurate than the results determined from optical data. Though the FIR-LMR technique has been successful for the investigation of a number of atomic structures, the lack of close coincidences with laser lines has prevented the measurement of important fine structure intervals *e.g.*, in the ground state of Si I, S I or N II.

5. Hyperfine Structures, Isotope Shifts and Zeeman Effect

The high resolution which is obtainable with the FTS in the infrared region makes possible the observation of hyperfine structures and isotope shifts. The consideration of such effects is important for investigating some solar profiles *e.g.*, for deducing abundances, as underlined recently by Kurucz (1992). The importance of isotope shift for interpreting the infrared lines of nickel in the photospheric spectrum has been emphasized by Brault and Holweger (1981).

Many observed hypermultiplets are adequately represented by the well known Casimir formula. In Al II, it was shown by Biémont and Brault (1987) that the observed structures for $ns-n'p$ transitions were correctly reproduced by this formula while the observations for $np-n'd$, $nd-n'f$ and $nf-n'g$ transitions were not. Hyperfine structure profiles in the infrared have been the subject of recent experimental or theoretical investigations in Al II (Biémont and Brault, 1987), In I (George *et al.* 1990), Sb I (Hassini *et al.*, 1988), Bi I (George *et al.* 1985), Pr II (Ginibre, 1989*a,b*) and Pt II lines (Engleman, 1989). Many hyperfine profiles are also observed in the vanadium spectra which are presently analyzed in Liège. An example is represented in Figure 2.

Zeeman patterns were considered for aiding in the identification work or for determining g factors in Zr I (Taklif, 1990*b*) and in Pr II (Ginibre, 1989*a,b*).
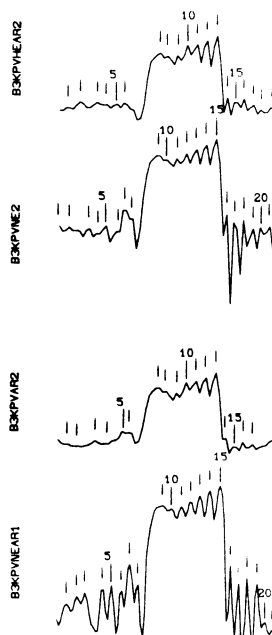
TABLE I
Far Infrared Measurements by the Laser Magnetic Resonance Technique

Ion	Transition	λ (μm)	σ (cm^{-1}) (FIR)		σ (cm^{-1}) (OPT)
^{12}C I	$2p^2\ ^3P_0 - ^3P_1$	609.13536(7)	16.416712(2)	A	16.40a
		609.1348(14)	16.41673(4)	B	
		609.1333(9)	16.41677(2)	C	
	$^3P_1-^3P_2$	370.4144(4)	26.99679(3)	B	27.00a
		370.4139(13)	26.99683(9)	C	
^{13}C I	$2p^2\ ^3P_0-^3P_1$				
	(F, F'=1/2–3/2)	609.13088(9)	16.416833(2)	A	
	=1/2–1/2)	609.13599(21)	16.416695(6)	A	
	$^3P_0-^3P_1$	609.1327(25)	16.41678(7)	B	
		609.131(2)	16.41682(7)	C	
	$^3P_1-^3P_2$	370.4119(5)	26.99697(3)	B	
		370.413(2)	26.9969(1)	C	
^{12}C II	$2p\ ^2P^o_{1/2}-^2P^o_{3/2}$	157.74093(11)	63.39509(4)	D	63.42a
^{13}C II	$2p\ ^2P^o_{1/2}-^2P^o_{3/2}$	157.74019(17)	63.39538(7)	D	
	(F, F'=1–2)	157.74681(19)	63.39273(8)	D	
	=1–1)	157.7742(8)	63.3817(3)	D	
	=0–1)	157.70665(12)	63.40887(5)	D	
^{14}N I	$2p^3\ ^2D^o_{3/2}-^2D^o_{5/2}$				
	(F,F' =1/2–3/2)	1145.6209(4)	8.728891(3)	E	8.713b
	=3/2–5/2)	1146.4477(4)	8.722596(3)	E	
	=5/2–7/2)	1147.4900(2)	8.714673(2)	E	
^{14}N II	$2p^2\ ^3P_1-^3P_2$	121.89806(7)	82.03576(5)	F	82.1b
^{15}N II	$2p^2\ ^3P_1-^3P_2$	121.89750(9)	82.03614(6)	F	
^{16}O I	$2p^4\ ^3P_2-^3P_1$	63.183717(27)	158.26862(7)	G	158.265d
		63.183671(2)	158.268741(5)	H	
	$^3P_1-^3P_0$	145.52548(8)	68.71649(4)	J	68.712d
		145.525439(7)	68.716508(3)	H	
^{18}O I	$2p^4\ ^3P_1-^3P_0$	145.52474(8)	68.71684(4)	J	
^{24}Mg I	$3s3p\ ^3P^o_0-^3P^o_1$	498.592792(3)	20.0564472(1)	K	20.059e
	$^3P^o_1-^3P^o_2$	245.6157(6)	40.7140(1)	M	40.714e
^{25}Mg I	$3s3p\ ^3P^o_0-^3P^o_1$				
	(F, F' =3/2–5/2)	498.17611(1)	20.0732226(5)	N	
	=5/2–5/2)	498.46601(1)	20.0615484(5)	N	
	=7/2–5/2)	498.89415(1)	20.0443321(5)	N	
^{26}Mg I	$3s3p\ ^3P^o_0-^3P^o_1$	498.591377(3)	20.056504(1)	K	
^{28}Si I	$3p^2\ ^3P_0-^3P_1$	129.68173(4)	77.11187(2)	P	77.115c

References: a) Moore (1970); b) Moore (1975); c) Moore (1967); d) Moore(1976); e) Martin and Zalubas (1980) A) Yamamoto and Saito (1991); B) Cooksy et al. (1986c); C) Saykally and Evenson (1980); D) Cooksy et al. (1986a); E) Bogey et al. (1989); F) Cooksy et al. (1986b); G) Saykally and Evenson (1979); H) Zink et al. (1991); J) Davies et al. (1978); K) Bava et al. (1983); M) Inguscio et al. (1985); N) Godone et al. (1984); P) Inguscio et al. (1984).

V I

2 isotopes ^{50}V (0.3%)
and ^{51}V(99.7%)

F - F'	Int(LS)
1 - 2	18.9*
2 - 3	24.9*
2 - 2	6.7
3 - 4	32.7*
3 - 3	10.9
3 - 2	0.7
4 - 5	42.2*
4 - 4	13.6
4 - 3	1.1
5 - 6	53.6*
5 - 5	14.7
5 - 4	1.1
6 - 7	66.9*
6 - 6	14.2
6 - 5	0.9
7 - 8	82.3*
7 - 7	11.8
7 - 6	0.6
8 - 9	100.*
8 - 8	7.1
8 - 7	0.2

$\sigma_{calc} = 5132.010 \ cm^{-1}$

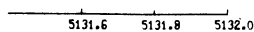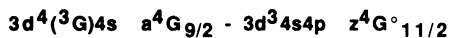$3d^4(^3G)4s \ a^4G_{9/2} - 3d^34s4p \ z^4G°_{11/2}$

5131.6   5131.8   5132.0

Fig. 2. Example of HFS in FTS vanadium spectra. The structure of the $3d^4(^3G)4s \ a^4G_{9/2}$ $- 3d^34s4p \ z^4G°_{11/2}$ transition is illustrated. The most intense components are due to $\Delta F = 1$ transitions. The wavelength scale is in cm^{-1}.

6. Atomic Transition Probabilities

Transition probabilities for numerous infrared atomic lines have been calculated as part of two extensive projects developed during the past few years (Seaton, 1987, Kurucz, 1991). Through the combination of radiative lifetime measurements by laser techniques and of branching ratio determinations from FTS spectra, a large number of f-values have been obtained for Fe I (0.225–2.666 μm; O'Brian *et al.* 1991), Mo I (up to 1.0565 μm; Whaling and Brault, 1988) and Ce I (Bisson *et al.*, 1991). In view of their astrophysical importance, N I and O I have been investigated in detail by Hibbert *et al.* (1991*a,b*) using the CIV3 method. Accurate oscillator strengths have been obtained for many infrared lines and the f values have been used for refining the solar abundances of these elements (Biémont *et al.*, 1990, 1991) from a sample of near infrared lines. The results obtained ($A_N = 7.99 \pm 0.04$ and $A_O = 8.86 \pm 0.04$, in the usual logarithmic scale) are in agreement with the corresponding abundances deduced from molecular lines (see, *e.g.*, Grevesse *et al.*, 1992). Similar calculations for C I will be published soon.

Acknowledgements

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