HIGH RESOLUTION INFRARED SPECTROSCOPY OF TRANSIENT MOLECULES

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INTRODUCTION

Driven by advances in instrumentation, the field of high resolution infrared spectroscopy has expanded remarkably in recent years. A selection of a small number of topics is necessary to keep this review within the page limits. It seems to me that the topic of high resolution infrared spectroscopy divides itself into the following (somewhat overlapping) categories:

I. Instrumentation and techniques
II. Spectra of molecules
   A. Stable molecules, e.g. CH_4
   B. Semistable molecules, e.g. HCP
   C. Van der Waals and hydrogen-bonded molecules, e.g. $(HF)_2$
   D. High temperature molecules containing metals, e.g. NaF
   E. Nonmetal free radicals and transient molecules, e.g. CN
   F. Ions, e.g. HCO^+.

In this review the topics of instrumentation (I), high temperature molecules (II D), free radicals (II E), and a few arbitrary selections from the semi-stable molecule category (II B) are discussed. Furthermore, only gas-phase vibration-rotation transitions of ground electronic states are included. Such topics as infrared electronic transitions [e.g. SiC (1)], pure rotational transitions [e.g. OH (2, 3)], and vibration-rotation transitions in excited electronic states [e.g. $a^1\Delta$ state of SO (4)] are excluded. The detection of

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vibration-rotation transitions for the study of reaction kinetics rather than spectroscopy is, in general, also not covered.

There have been several related previous reviews of infrared spectroscopy of transient molecules. In 1983 Robiette & Duncan reviewed "High Resolution Vibration-Rotation Spectroscopy" (5), including transient molecules. Over the years, Hirota and coworkers have reviewed this topic several times and Hirota has written a book (6-10). In 1980, McDowell wrote a very thorough review of "Vibrational Spectroscopy Using Tunable Lasers" (11). Mooradian (12) and Oka (13) have written similar reviews. Kroto (14) and Westwood (26) have written very good articles about their work with semistable molecules. Finally, the extensive reviews by Jacox are very helpful (306).

INSTRUMENTATION AND TECHNIQUES

Remarkable advances in infrared technology have made the spectroscopy of transient molecules possible. Work in the infrared region of the electromagnetic spectrum suffers some practical and some inherent difficulties compared to the microwave and the visible regions. Perhaps the most serious intrinsic limitation on infrared spectroscopy is that vibration-rotation transition dipole moments are typically 0.1 D, whereas permanent dipole moments and electronic transition dipole moments often exceed 1 D. Although vibration-rotation transitions are relatively weak, all molecules except homonuclear diatomics have allowed electric-dipole infrared transitions. The universal applicability of vibration-rotation spectroscopy is an attractive feature of infrared work.

A more serious practical limitation of infrared spectroscopy is the lack of high power, widely tunable, c.w. infrared lasers comparable to visible dye lasers or microwave oscillators (11). Color center lasers cover the wavelength region to the blue of 3 μ, and diode lasers are slowly improving their spotty performance, but the infrared world is still waiting for the equivalent of a visible dye laser. In the interim period, schemes based on the nonlinear optical properties of materials such as difference frequency lasers, tunable sideband lasers, and Raman shifting pulsed visible lasers are popular.

Until a few years ago, infrared detectors and materials were generally inferior to those available in other spectral regions. Numerous modern practical applications of infrared technology, particularly military applications, have changed this. Infrared detectors now have high quantum efficiencies [e.g. 70% for InSb for $\lambda < 5\ \mu$ or 30% for Cu:Ge for $\lambda < 28\ \mu$ (15)]. High quality infrared materials and optical coatings are readily available from many suppliers. Of course, the room temperature black-

body radiation curve, plotted as a function of wavelength, still peaks at 10 μ and interferes with infrared measurements. Nonetheless, the careful design of cold apertures to limit the field of view and the use of cold band pass filters can greatly diminish the problems of thermal background radiation.

Fourier Transform Spectroscopy

The principles and advantages of Fourier transform spectroscopy have been described in many reviews (e.g. 16a,b, 17). Robiette & Duncan (5) summarized the state of high resolution Fourier transform spectroscopy in 1983. I mention only the advances since 1983.

For the spectroscopy of transient molecules, the main advantage of Fourier spectroscopy over classical grating spectroscopy is the increase in sensitivity. This advantage, however, may not persist for much longer. The combination of a cold grating spectrometer (cryogenic echelle spectrograph) with an infrared array detector (18a,b) will probably replace the Fourier transform spectrometer for ultrasensitive astronomical work of very faint sources. Other convenient advantages of Fourier spectroscopy, including wide spectral coverage and a precise, accurate wavenumber scale, will ensure its survival.

Both custom-built and commercial interferometers are available for high resolution laboratory spectroscopy. The custom instruments at Kitt Peak operated by the National Solar Observatory (J. Brault) and at Orsay operated by Laboratoire Aimé Cotton (G. Guelachvili) continue to be successful at recording the infrared vibration-rotation spectra of transient molecules. Other custom high resolution instruments available include the AFGL interferometer (M. B. Esplin and M. Hoke), the other Laboratoire Aimé Cotton spectrometer (J. Verges), the Imperial College Instrument (A. Thorne), the Finnish instrument (J. Kauppinen), the Los Alamos interferometer (B. Palmer and R. McDowell), the Danish Raman instrument (J. Bendtsen and S. Brodersen), the Université Pierre et Marie Curie instrument (A. Valentin), and the Florence far IR interferometer (B. Carli).

Perhaps the largest impact will be made by the three commercial high resolution instruments. The interferometer made by Chelsea Instruments (FT 500) works only in the visible and ultraviolet regions of the spectrum. The Bruker HR 120 and the Bomen DA3/DA8 cover the far infrared to ultraviolet regions of the spectrum. The Bomen has a maximum optical path difference of 2.5 m ["resolution" $\sim 0.6/L = 0.002$ cm^{-1} (15)], while the Bruker offers twice the path difference (5.0 meters) and correspondingly improved resolution. The two instruments, in general, seem to be comparable in price and performance. The extra factor of two in resolution provided by the Bruker instrument is important for the far and mid-IR

spectra of stable molecules. The Bomem instrument can also be modified to achieve the same resolution as the Bruker (19). For the spectroscopy of transient molecules, resolution is usually second to sensitivity in importance. The low concentrations of transient molecules push the instrumentation to the limits of sensitivity, and often some sacrifice in resolution needs to be made in order to obtain a spectrum.

FOURIER TRANSFORM EMISSION SPECTROSCOPY   In the visible and ultraviolet regions of the spectrum, emission spectroscopy is the method of choice for the detection of transient molecules. In the infrared region, the emission rates (Einstein A factors) are much smaller, and the radiative lifetimes (the reciprocal of the Einstein A factor) much longer. For example, for the infrared fundamental vibration of CH, the theoretical dipole moment function (20) $\mu = 1.43 - 1.64(r - r_o)$ D and the harmonic approximation give a transition dipole moment of -0.134 D, an Einstein A of 115 sec^{-1} and a vibrational lifetime of 8.7 msec (21, 22). In spite of the experimental difficulties, it has proved possible to detect the vibration-rotation emission spectra of many hydrides, including CH (Figure 1), SH, NH, PH, OH, SiH, BH, AlH, and TeH (Tables 1, 5). Hammer et al have observed the emission spectrum of FO formed in the $F+O_3$ flame (23).

In an important experiment, H. Uehara et al (24) have observed the emission spectrum of the GeS ($X^1\Sigma^+$) near 17 μ (574 cm^{-1}) at 900K. The same group also saw InF emission at 19 μ (535 cm^{-1}) from the $In+InF_3$ reaction (25). We have confirmed that emission measurements are simple and convenient by detecting SiS (Figure 2) under similar experimental
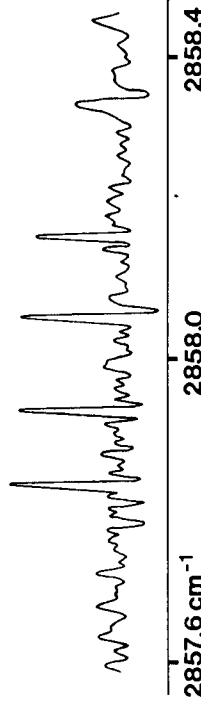
CH   1-0   R(4)

2857.6 cm^{-1} 2858.0   2858.4

Figure 1 The R(4) emission line of the fundamental band of CH (141). For each value of N there is a characteristic quartet structure because of the Hund's case (b) $X^2\Pi$ ground state of CH.
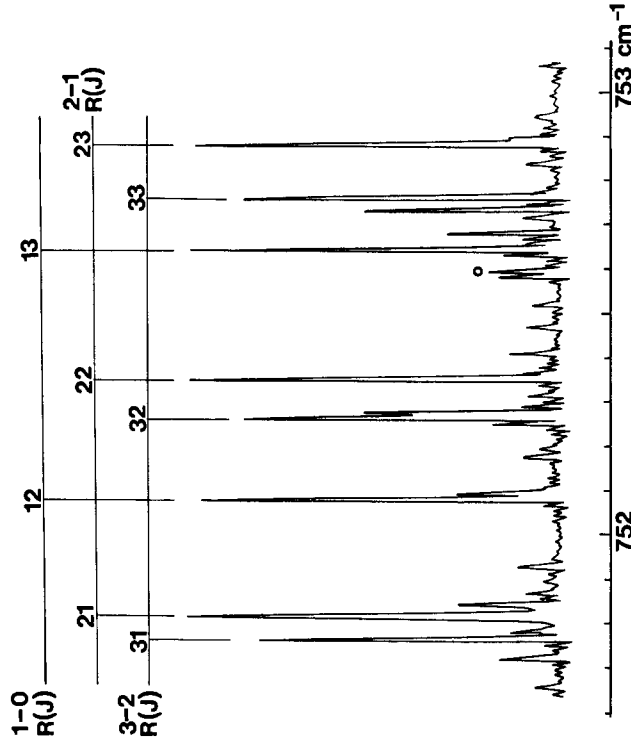
752   753 cm^{-1}

Figure 2 The vibration-rotation emission spectrum of SiS near 13 μ formed in the Si+SiS$_2$ reaction (C. Frum, P. F. Bernath, work in progress). For the main isotopomer $^{28}Si^{32}S$, the 1-0 to 7-6 bands were observed, while three bands each for the minor isotopomers, $^{29}Si^{32}S$, $^{30}Si^{32}S$, $^{28}S^{34}S$, were found. All the lines in this figure can be assigned.

conditions with the National Solar Observatory instrument (C. Frum, P. F. Bernath, work in progress). The production of hot SiS molecules is the result of the Si(s)+SiS$_2$ reaction in a tube furnace. The long wavelength emission results for GeS (24), InF (25), SiS (C. Frum, P. F. Bernath), and FO (23) are particularly significant because they suggest that if suitable reactions can be found, Fourier transform emission spectroscopy of vibration-rotation transitions can be a very powerful tool for the discovery of new molecules.

FOURIER TRANSFORM ABSORPTION SPECTROSCOPY   The main difficulty with infrared absorption spectroscopy of transient molecules is obtaining and maintaining a sufficiently large path length–concentration product. For high temperature molecules this is usually achieved by heating in a tube furnace to obtain a high concentration (10^{14}–10^{16} molecules/cm^3) in a short path length (~ 1 meter). Unfortunately, continuous free radical concentrations are typically much lower (10^{10}–10^{13} molecules/cm^3), so

correspondingly longer path lengths are required (~ 100 meters). The pioneers in this work are A. Maki for high temperature molecules and the group headed by C. Howard for free radicals.

The experiments of the Boulder group are particularly significant (27). The free radicals are made by chemical reactions, typically with F (28) or Cl atoms, and pumped rapidly with a 500 L/sec Roots blower through a long path multiple reflection White cell (27). For example, to record the antisymmetric stretch, v_3, of N_3 near 1645 cm^{-1}, the reaction:

$$Cl + HN_3 \rightarrow N_3 + HCl$$
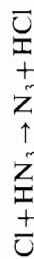
was utilized (29).

The selective infrared detection of paramagnetic molecules by Zeeman modulation is a well established technique (e.g. 30). Recently, Gudeman and coworkers have applied Zeeman modulation (31) and polarization modulation (32) to the Fourier transform spectroscopy of paramagnetic species. Modulation techniques will not, in general, increase the sensitivity of the Fourier transform technique, but they will provide a very important discrimination against, for example, unwanted diamagnetic precursor molecules.

TIME-RESOLVED FOURIER TRANSFORM EMISSION SPECTROSCOPY   The detection of transient infrared emission of free radicals with a Fourier transform spectrometer is a promising new technique (33). A pulsed ultraviolet laser photodissociates a precursor molecule, for example C_2H_2 to make C_2H (34) or CH_3I to make CH_3. In this pulsed mode, the initial concentrations of hot free radicals can be very large (10^{16} molecules/cm^3 or more). By carefully timing the firing of the photolysis laser with respect to the data acquisition time, an infrared emission spectrum at a set time delay after photolysis is recorded (33). Although no new spectra of free radicals have been recorded yet, mainly because the current practitioners are more interested in kinetics, the technique holds great promise for spectroscopic studies.

Diode Laser Spectroscopy

Tunable semiconductor diodes made from Pb salts such as $Pb_{1-x}Sn_xTe$ provide tunable infrared radiation from 360 cm^{-1} to 3500 cm^{-1} (2.8 μ to 28 μ) (11, 35). Unfortunately, each diode has a total range of perhaps 100 cm^{-1} and within that interval the coverage is perhaps 30%. There have been steady improvements in the range, coverage, output power, and mode quality of the devices in recent years. For example, the application of molecular beam epitaxial growth techniques allows the manufacture of diodes that operate above 77K (36). There is, however, still too much art and not enough science in the manufacture of laser diodes.

Diode lasers are widely used for absorption spectroscopy because they can be extremely sensitive. For example, Carlisle et al (37) have demonstrated quantum noise-limited frequency modulation spectroscopy with a sensitivity ($\Delta I/I$) of 10^{-7}, although a "typical" routine value is 10^{-4}. In contrast, a $\Delta I/I$ of 10^{-3} is typical for Fourier transform absorption spectroscopy. The sensitivity of diode lasers is responsible for their widespread use in spectroscopy, but the lack of complete spectral coverage is a serious and frustrating defect. Rotational assignments in the spectra of new molecules, particularly asymmetric tops, are difficult if only a partial spectrum is available.

A typical diagram of a diode laser spectrometer is shown in Figure 3. The heat pipe oven is suitable for high temperature molecules such as alkali halides, for example NaF (38), or metal hydrides such as BiH (39). The pioneering work by A. Maki (see Tables 2 and 3) on high temperature molecules and the extensive list of metal hydrides (see Table 1) studied by H. Jones and coworkers are particularly notable.

If the hot cell is replaced by an electrical discharge cell, then the spectra of many free radicals can be recorded. Free radicals can be made with
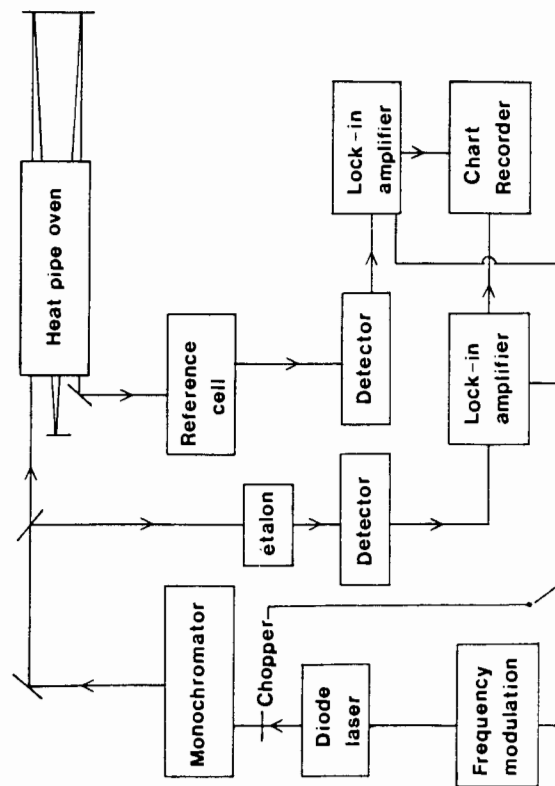

Figure 3   A typical experimental diagram for a diode laser spectrometer (91). The monochromator serves as a mode selector and for approximate frequency calibration of the diode. The calibration of the spectrometer is accomplished with a reference gas and an etalon for relative frequency calibration. The reference cell is placed in the same path as the unknown molecule simply to avoid using a third lock-in amplifier and detector.

D.C., low frequency A.C. (60 Hz neon sign transformer), radio frequency, and microwave electrical discharges. A large hollow cathode cell developed by van den Heuvel & Dymanus (40) is a particularly effective source for the production of free radicals and molecular ions. The cathode of this cell can be cooled with liquid nitrogen, and discharge modulation of molecular concentrations is very conveniently implemented.

Infrared kinetic spectroscopy is a powerful method for the observation of the spectra of free radicals and for studies of reaction kinetics (6). The ultraviolet light from an excimer laser is a convenient source of radiation for the photolysis of a precursor molecule such as HCCH to yield a free radical such as CCH (41). The transient infrared absorption of a diode laser beam is monitored with a fast infrared detector and a gated integrator. The virtues of time-resolved techniques have already been mentioned in the discussion of time-resolved Fourier transform spectroscopy. In addition to the diode laser, the color center laser (42) or a difference frequency spectrometer (43) can be used as the source of infrared radiation.

Most measurements of the infrared spectra of high temperature molecules use a simple tube furnace made of stainless steel, alumina, or carbon (King furnace). Very recently the Broida oven (44), a high temperature flow reactor, has been utilized by Hedderich & Blom (125–128) for infrared diode laser measurements. Hedderich & Blom (see Table 3) have recorded the diode laser spectra of the alkaline earth oxides, MgO, CaO, SrO, and BaO. These molecules were made by the reactions of metal vapors with an N_2O oxidant. This is an important advance because the alkaline earth monoxides are difficult to vaporize directly from their refractory solids.

Color Center Laser Spectroscopy

Various kinds of defects in alkali halide crystals result in the formation of color centers or F-centers. These color centers can be pumped by flash lamps or lasers (such as Nd:YAG, argon ion, and krypton ion) to provide widely tunable output from 0.5–3.4 μ (45). Many different crystals and different types of defects are required for this coverage, but only the long wavelength region, where dye lasers and tunable solid state lasers (e.g. Ti:sapphire) do not operate, are useful. Note that tunable solid state lasers can operate in the infrared, for example Co:MgF_2 covers the 1.13–2.08 μ region (12, 46).

The main drawback to the color center laser is the lack of mid-infrared wavelength coverage. Typically, only high frequency hydride fundamental vibrations (CH, NH, and OH stretches) and the weaker overtones of lower frequency vibrations are accessible. For example, the OH, NH (42), NH_2 (42), and C_2H (see Table 4) spectra have been detected by magnetic rotation spectroscopy or infrared kinetic spectroscopy with a color center laser.

CO_2, N_2O, and CO Laser Spectroscopy

A number of excellent line tunable lasers are available in the infrared. The CO_2 and N_2O lasers at 10 μ and the CO laser at 5 μ are the most commonly used gas lasers for infrared spectroscopy. These relatively cheap and reliable lasers have high output powers and excellent mode quality but are not continuously tunable. In order to be useful for spectroscopy, either the molecule must be tuned into resonance with the fixed frequency laser or the laser system must be modified to provide tunable radiation.

The CO_2 laser can be made somewhat more tunable by pressure-broadening the gain curve and confining the gas discharge in a narrow waveguide (11, 49). Almost complete coverage of the 10 μ region can be achieved by tunable side band generation as developed by Magerl et al (50, 51). The fixed frequency CO_2 laser beam and tunable microwave radiation are mixed in a nonlinear crystal such as CdTe to provide tunable infrared radiation. Frequency synthesis in a GaAs waveguide is also possible (52). Tunable far infrared radiation is provided by difference frequency mixing of two different CO_2 laser lines (53). The spin-flip Raman laser in which InSb pumped by a CO laser is used (11, 54) provides tunable radiation near 5 μ but is difficult to operate.

In general, however, it is simpler to use an electric or a magnetic field to tune the transition frequency of the molecule into resonance with a fixed frequency laser than to make the laser tunable. Laser electric resonance and laser magnetic resonance (55, 56) are popular techniques for high resolution spectroscopy.

In principle, laser electric resonance can be applied to all polar molecules, but, in practice, the technique is confined mainly to stable molecules. The problem is that electrical discharges are often used to make free radicals, simultaneously creating ions and free electrons. The presence of ions and electrons makes the operation of the Stark plates very difficult because of electrical breakdown; however, with some difficulty, Landsberg et al recorded the laser Stark spectrum of HCO (57).

Laser magnetic resonance relies on the Zeeman effect to tune the molecular transitions of paramagnetic molecules into resonance with the laser. The technique is very sensitive and ideally suited to the study of high resolution spectra of free radicals (55, 56). In fact, the main difficulty with laser magnetic resonance is the assignment of the complex spectra, not the acquisition of the spectra.

Recently, Urban and coworkers have modified the "standard" intra-cavity laser magnetic resonance spectrometer (e.g. 58). By mounting the discharge cell external to the CO laser cavity and using the Faraday effect to detect the molecular transitions, they improved the sensitivity by more

than two orders of magnitude (59, 60). With this instrument they have recorded the spectra of NiH, CoH, SnH, SiH, SD, and NCO (see Tables 1, 5 and 10).

Miscellaneous Techniques Based on Nonlinear Optics

Tunable infrared radiation can be generated by difference-frequency mixing two c.w. visible dye lasers in $LiNbO_3$ or $LiIO_3$ crystals. Pine has developed (61–63) a tunable laser spectrometer that covers the 2.2–4.2 μ region by using $LiIO_3$. Bawendi & Oka developed a spectrometer based on $LiIO_3$ to cover the 2–5.5 μ wavelength range (64, M. Bawendi, T. Oka, in preparation; see also 65). Although only a few tens of microwatts of c.w. power are available from difference frequency mixing in $LiNbO_3$ (much less for $LiIO_3$), the technique provides complete wavelength coverage. Difference frequency spectrometers have been applied mainly to ions and van der Waals molecules but a few free radicals such as SH, NH, HO_2, and CH_3 have been detected (see Tables 4, 5, 8 and 9).

Several other techniques provide tunable infrared radiation with pulsed lasers. For example, near infrared lasers can be Raman-shifted using H_2 gas into the infrared (12, 66). Resonantly enhanced Stokes shifting of visible lasers into the infrared is also possible with metal vapors such as Cs (67, 68). Four-wave mixing in metal vapors (11, 12) can also generate tunable infrared radiation.

The optical parametric oscillator (OPO) is also a good source of radiation for pulsed infrared work. A variety of nonlinear crystals and pump lasers can be used to make an OPO, but $LiNbO_3$ pumped by a Nd:YAG laser is a popular choice (69–71). The main limitation of pulsed lasers for high resolution spectroscopy is that the laser linewidths are too large, typically 0.04–1 cm^{-1}. Much narrower linewidths are possible with some effort, however, since the intrinsic uncertainty limit for a typical 10 nsec pulse is 0.0005 cm^{-1}.

HIGH TEMPERATURE MOLECULES

What is a high temperature molecule? Unfortunately, there is no perfectly clear and infallible definition of a high temperature molecule apart from the obvious requirement of a furnace for molecule production. Typically, high temperature molecules contain metal atoms, but molecules such as C_2, C_3, and SiC_2 could also be included because they can be made in high temperature furnaces. So far, not a single high resolution vibration-rotation spectrum of a metal-containing polyatomic molecule has been published. Uehara and coworkers have recorded the diode laser spectrum of NaOH during the course of their work with NaCl (72), but this work

has not appeared in print yet. Our review is, therefore, confined to high temperature diatomic molecules.

Metal Hydrides and Deuterides

Table 1 summarizes the observed infrared vibration-rotation spectra of metal hydrides. By the time this review appears, Table 1 will be greatly out of date because of the rapid progress in this area. The research group headed by H. Jones is particularly prolific. Most of the metal hydride spectra were recorded with a diode laser spectrometer and a tube furnace cell for molecule production. A typical diode laser spectrum of a metal hydride, BiH, is provided in Figure 4. For only a few molecules, LiH, NaH, AlH, TeH, and CuH, have spectra been recorded with a Fourier transform spectrometer. The AlH, TeH, and CuH spectra were recorded in emission, whereas SnH, CoH, GeH, SeH, SeD, and NiH were recorded by laser magnetic resonance spectroscopy. The assignment of the laser magnetic resonance spectra and the diode laser spectra are greatly aided by the prior observation of electronic transitions.
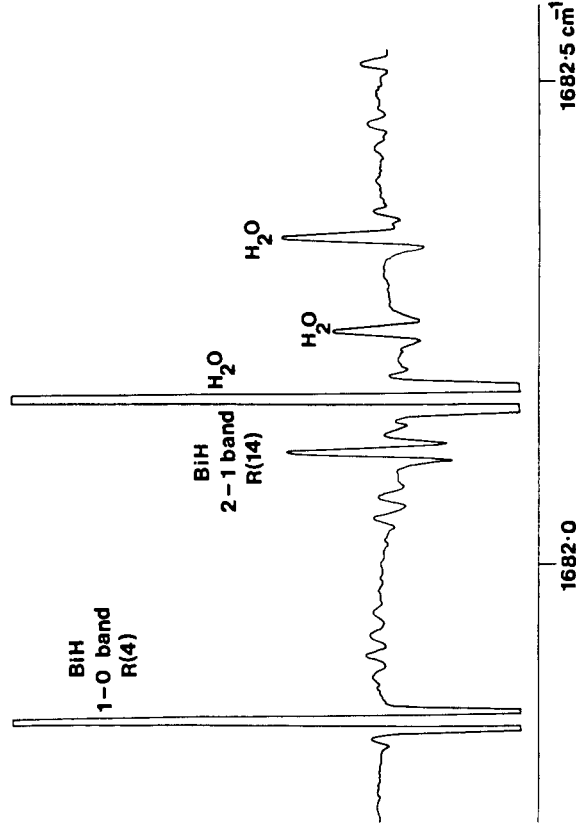

Figure 4 A "typical" spectrum from the diode laser study of BiH (91). The BiH was made in a hot cell by the reaction of Bi vapor with 25 torr of hydrogen at 1000°C. The molecular lineshape is a second derivative because the technique of frequency modulation with lock-in detection at twice the modulation frequency was used. This modulation scheme gives a flatter baseline than lock-in detection at the modulation frequency.

Metal Halides

The vibration-rotation spectra of high temperature metal halides are summarized in Table 2. The principal contributors to the work in Table 2 are A. Maki and coworkers, who recorded absorption spectra in a tube furnace with a diode laser spectrometer and, more recently, with a Fourier transform spectrometer. A typical diode laser spectrum of $^6Li^{79}Br$, $^7Li^{79}Br$, and $^7Li^{81}Br$ recorded in the first overtone ($\Delta v = 2$) region is displayed in Figure 5. Slightly more than half of the possible 20 nonradioactive alkali halides have been detected by vibration-rotation spectroscopy. The remaining alkali halides have rather small rotational constants and have their vibration-rotation fundamentals in the far infrared region. The InF molecule was recorded in emission from the reaction of InF$_3$ with In.

High Temperature Chalcogenides

So far, only a few high temperature oxides and sulfides have been detected by vibration-rotation spectroscopy (Table 3), all but one with $^1\Sigma^+$ ground

states. Yamada & Hirota (129) recently detected the fundamental vibrational band of the $X^2\Pi$ ground state of LiO with a diode laser. The alkaline earth oxides spectra were recorded by diode laser spectroscopy with a Broida oven. The group IV oxides and sulfides spectra were typically recorded in a tube furnace, although CS can also be made in an electrical discharge of CS_2 or the reaction of O atoms with CS_2. The SiO molecule was found in the spectra of sun spots. The GeS and SiS molecules were recorded by Fourier transform emission spectroscopy. These observations violate the conventional wisdom that emission work is not possible below the 1800 cm^{-1} InSb detector cutoff.

CARBON CHAIN MOLECULES AND HYDROCARBON FREE RADICALS

The pure carbon chain molecules C_3 and C_5 and the related hydrocarbon free radicals such as CH and CH_2 have been separated from the nonmetal transient molecules because they are of great interest in many diverse areas. These molecules are important in combustion, detonations, and propulsion, and are found abundantly in many extraterrestrial sources. In materials science they are important, for example, in the growth of diamond films.

The study of pure carbon molecules has recently become one of the more fashionable areas in science. The pivotal discovery of C_{60} and related fullerenes by Kroto et al (130) has inspired the work of many chemists, physicists, and astronomers. The smaller members of the C_n family are linear (although cyclic and bent forms may be low-lying in energy) rather than monocyclic or spheroidal (131). The smaller linear members of this family such as C_3 and C_5 have been characterized by high resolution vibration-rotation spectroscopy.

Although the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ (cometary) electronic transition of C_3 is well-known (132), until recently on high resolution infrared spectra were available. The antisymmetric stretching mode at 2040 cm^{-1} was detected independently in the laboratory by diode laser spectroscopy (133, 134) and in the Fourier transform spectrum of a carbon star (135). The strong absorption spectra of C_3 observed in the carbon star (Figure 6) led Bernath et al to search for C_5 (Figure 7). In this case, the astronomical detection (139) of C_5 preceded (by a few days) the laboratory observations (136, 138). The low resolution matrix isolation infrared spectra (167, 168) of C_3 and C_5 were vital to the high resolution work.

The diode laser spectrum of C_5 recorded by Moazzen-Ahmadi et al (136, 137) was recorded in an acetylene/He discharge in a Nijmegen-style hollow cathode cell (40). The Berkeley group (138) recorded their cold spectrum
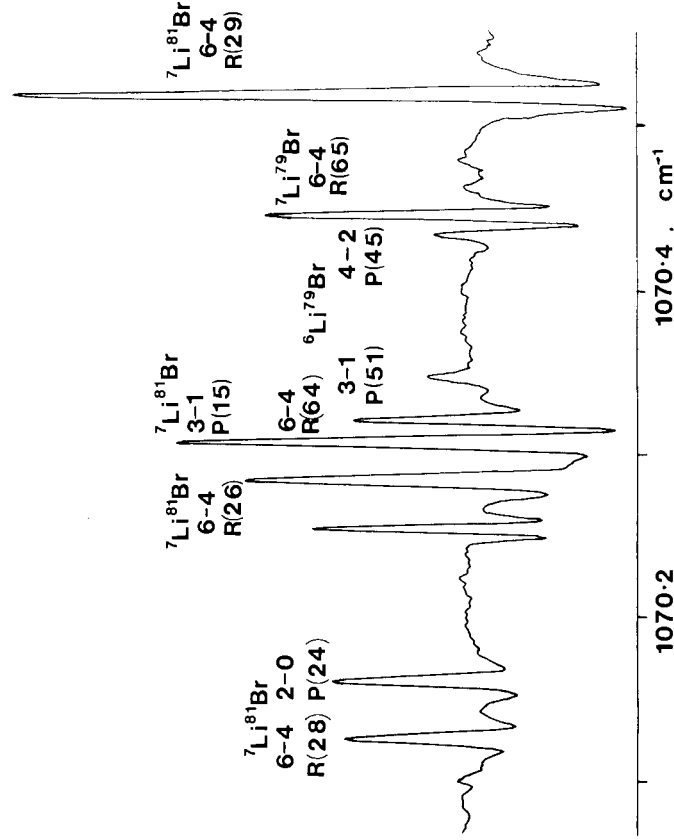

Figure 5 A portion of the LiBr vibration-rotation spectrum recorded with a diode laser spectrometer (104). The LiBr molecule was made by simply heating the salt to 800°C. The spectrum was very dense because at this high temperature many vibrational and rotational levels are populated and because there are four isomeric forms of LiBr, $^6Li^{81}Br$, $^7Li^{81}Br$, $^6Li^{79}Br$, and $^7Li^{79}Br$.

[Peak labels in figure:]
$^7Li^{81}Br$ 2-0 6-4 R(28) P(24)

$^7Li^{81}Br$ 6-4 R(26)

$^7Li^{81}Br$ 3-1 P(15)

$^6Li^{79}Br$ 6-4 R(64)

$^6Li^{79}Br$ 3-1 P(51)

$^7Li^{79}Br$ 4-2 P(45)

$^7Li^{79}Br$ 6-4 R(65)

$^7Li^{81}Br$ 6-4 R(29)
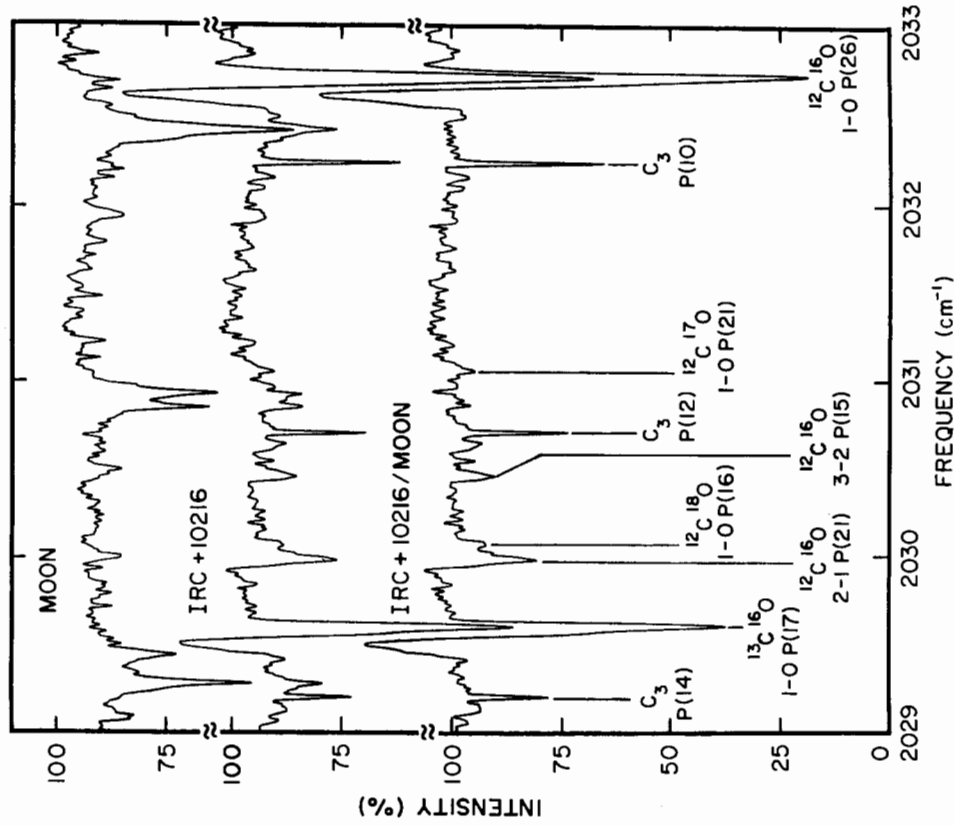
1070·2   1070·4   cm⁻¹

Figure 6　This is an infrared absorption spectrum of the carbon star, IRC+10216 (135). The *top panel* is the spectrum of the moon, which contains only atmospheric absorption features at this wavelength. The *middle panel* is the spectrum of the star, while the *bottom panel* is the ratio of the middle spectrum to the top spectrum. This normalization removes the atmospheric absorptions from the stellar spectrum. Note the strong CO features with peculiar and characteristic lineshapes. The CO occurs throughout the expanding stellar envelope, whereas C_3 occurs in only the cold outer region.

of C_5 with a laser-vaporization, jet expansion source. The application of free jet expansion technology to the infrared spectroscopy of transient molecules is an important innovation. Recently, Curl et al succeeded in recording the infrared spectrum of cold NH_2 made by excimer laser photolysis of NH_3 in a pulsed, free-jet expansion (169).
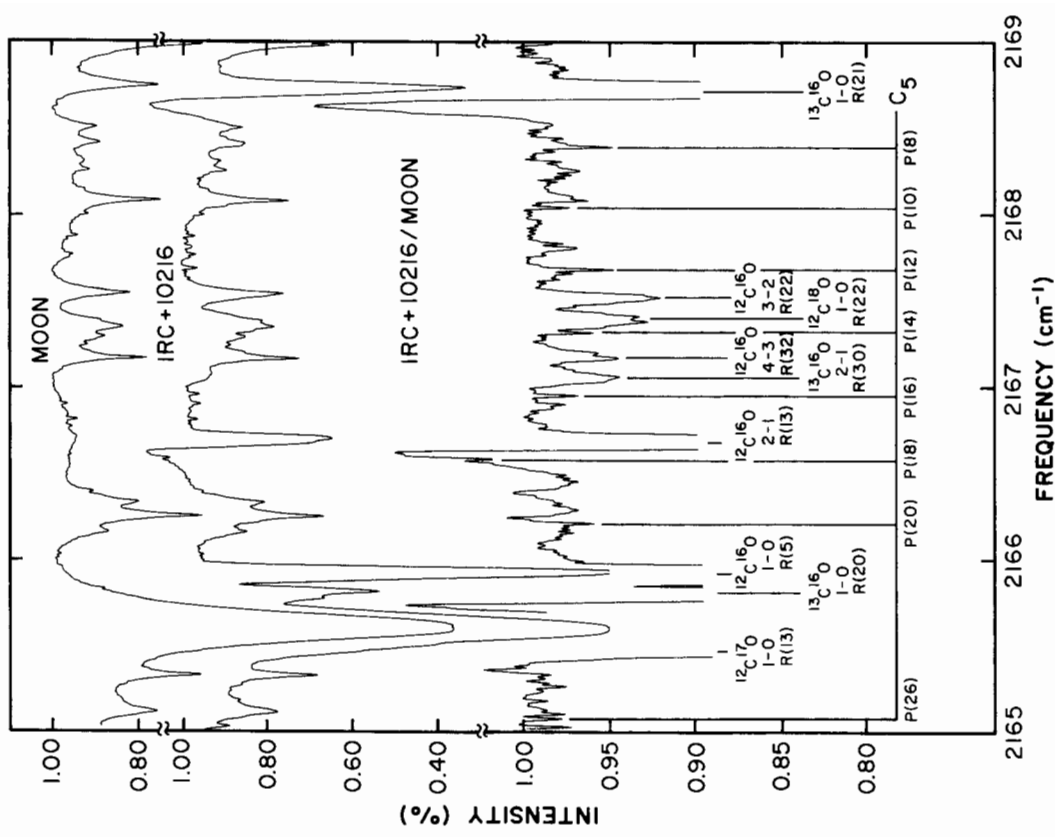
Figure 7　This is the absorption spectrum of C_5 in the carbon star, IRC+10216 (139). Figures 6 and 7 are quite similar, but the ratio spectrum, *bottom panel*, in this figure is expanded by a factor of 4.

The CH molecule was observed in absorption by difference frequency laser spectroscopy (140) and by Fourier transform emission spectroscopy (141) of hydrocarbon discharges (Figure 1). The Hund's case (b) $^2\Pi$ ground state of CH makes a characteristic quartet pattern for each value of N (Figure 1). Additional highly excited transitions of CH were observed by

Mélen et al in the ATMOS Fourier transform spectrum of the sun recorded from earth orbit (142).

The bending mode of CH_2, v_2, was discovered by CO_2 laser magnetic resonance spectroscopy in the ground $\tilde{X}^3B_1$ state (143). This pivotal work led to the assignment of the far infrared laser magnetic resonance spectrum (146, 171) and an accurate experimental determination of the singlet-triplet splitting (170, 171). CH_2 and CD_2 were also subsequently observed by diode laser spectroscopy (145, 148) and $^{13}CH_2$ by laser magnetic resonance (147). The v_1 and v_3 stretching modes of the ground state are, by accident, very weak and remain to be found. Note that v_1 and v_3 of the low-lying excited $\tilde{a}^1A_1$ state of CH_2 are known from difference frequency laser kinetic spectroscopy (172, 173).

The planar methyl radical, CH_3, is one of the more stable hydrocarbon radicals. The out-of-plane bending mode, v_2, of CH_3 and CD_3 has yielded to diode laser spectroscopy in which both laser kinetic (152, 153) and continuous electrical discharge (150, 151) techniques of molecule production were used. The antisymmetric stretching mode, v_3, was observed by difference frequency laser spectroscopy (Figure 8) near 3160 cm^{-1} (149).
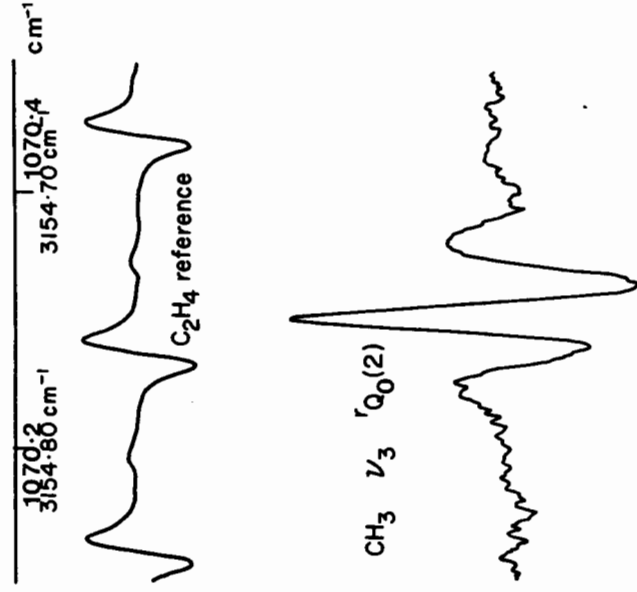

1070·2 ̄ 1070·4 cm^{-1}
3154·80 cm^{-1} 3154·70 cm^{-1}

C_2H_4 reference

CH_3 v_3 $^rQ_0(2)$

Figure 8 Antisymmetric C–H stretching mode (v_3) of CH_3 was recorded with Zeeman modulation (149). The CH_3 radical was made in a 60 Hz A.C. discharge in about 1 torr of di-tertiary-butyl-peroxide.

The infrared spectrum of C_2H was first detected by Carrick et al by color center laser spectroscopy of an acetylene/Ar discharge and of an argon discharge over polyacetylene deposits (154). Carrick et al (154) detected what is nominally the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ electronic transition of C_2H, which falls outside the scope of this review. The $\tilde{A}$–$\tilde{X}$ transition, however, is massively perturbed by Renner-Teller and vibronic interactions between the $\tilde{A}^2\Pi$ and $\tilde{X}^2\Sigma^+$ electronic states. In fact, the distinction between a vibrational transition and a vibronic transition is a moot point in the 3 μ CH stretch region. The Rice group has continued to work on the infrared spectrum of C_2H and C_2D as has the Okazaki group (Table 4).

Recently C_2H was detected by high resolution Fourier transform emission spectroscopy in an acetylene discharge by Vervloet & Herman (163), as well as by time-resolved photodissociation by Fletcher & Leone (34). The Fourier transform infrared spectrum of C_2H was also found in a carbon star by Keady & Hinkle (164).

The vinyl radical, CH_2CH, was detected by Kanamori et al by diode laser kinetic spectroscopy near 900 cm^{-1} (165). They found all of the rotational lines of the out-of-plane CH_2 wagging mode to be doubled by the in-plane C–H double minimum potential. Fluxional behavior may be common for many hydrocarbon free radicals. For example, Sears & Frye (166) have reported a very complex spectrum attributed to the ethyl radical, CH_3CH_2. The complications in the CH_3CH_2 spectrum seem to be associated with interacting inversion and torsional motions.

NONMETAL FREE RADICAL AND TRANSIENT MOLECULES

Diatomic Molecules

NONMETAL HYDRIDES   Table 5 summarizes the available spectroscopic information on nonmetal hydride molecules. In general, this class of molecules has been well-elucidated by many absorption and emission studies. All of the molecules in Table 5 have fundamental vibrations above the 1800 cm^{-1} cut-off of the InSb detector, so high quality, broad coverage Fourier transform emission spectra are readily available. Figure 9 shows a portion of the Fourier transform emission spectrum of PH recorded with the microwave discharge apparatus of Figure 10, while Figure 11 is the RKR potential curve derived from the $X^3\Sigma$ spectroscopic constants. The detection of NH, OH, and CH in the sun and stellar atmospheres is notable (142, 184, 189).

NONMETAL HALIDES   Table 6 presents the nonmetal halides for which vibration-rotation spectra are available. Most of the measurements are diode laser spectra recorded by the Okazaki group headed by Hirota.
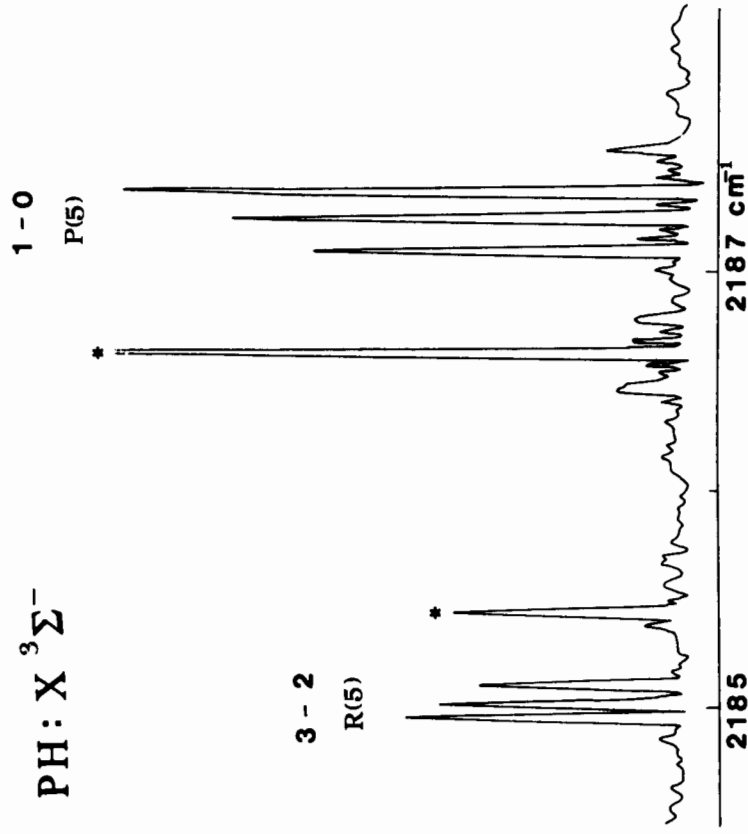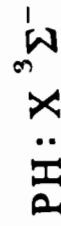
PH: X $^3\Sigma^-$

Figure 9   The emission spectrum of the PH radical was recorded in a microwave discharge of a white phosphorus vapor in hydrogen (187) (Figure 10). The vibration-rotation lines appear as triplets for each value of N because of the three spin-components of ground $X^3\Sigma^-$ state.

CF, FO, ClO, and BrO were detected by laser magnetic resonance spectroscopy. The high quality Fourier transform absorption measurements of CCl, FO, BrO, and ClO by the NOAA group are also notable. Hammer et al (23) also detected FO in emission from the chemiluminescent $F + O_3$ reaction.

NONMETAL CHALCOGENIDES   Table 7 lists the molecules for which vibration-rotation spectra have been detected. The derivatives of the semimetals As and Se have been included in Table 7 rather than in Table 3. For NSe, AsO, and SeO, the laser magnetic resonance measurements are of very high precision but not very extensive. The long-lived SO molecule has been studied by at least four different techniques, including, most recently, a Fourier transform absorption measurement.

Microwave   Discharge   Cell
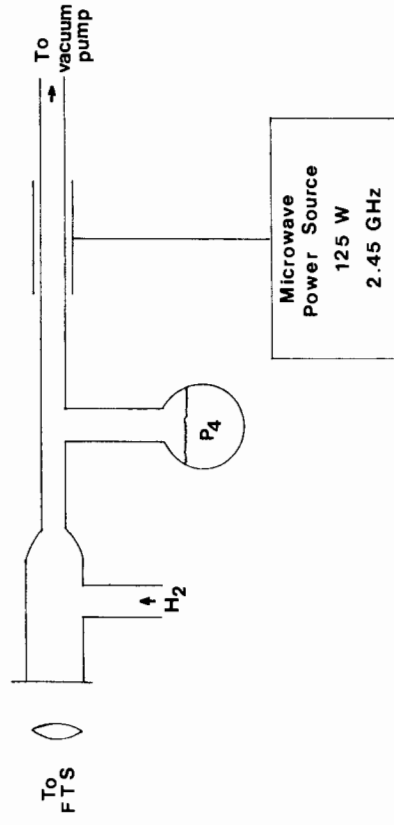
Figure 10   The PH molecule was made by flowing 0.5 torr of hydrogen and 40 mtorr of white phosphorus through a 2.45 GHz microwave discharge (187). The light from the plasma was imaged into the Fourier transform spectrometer with a single lens.
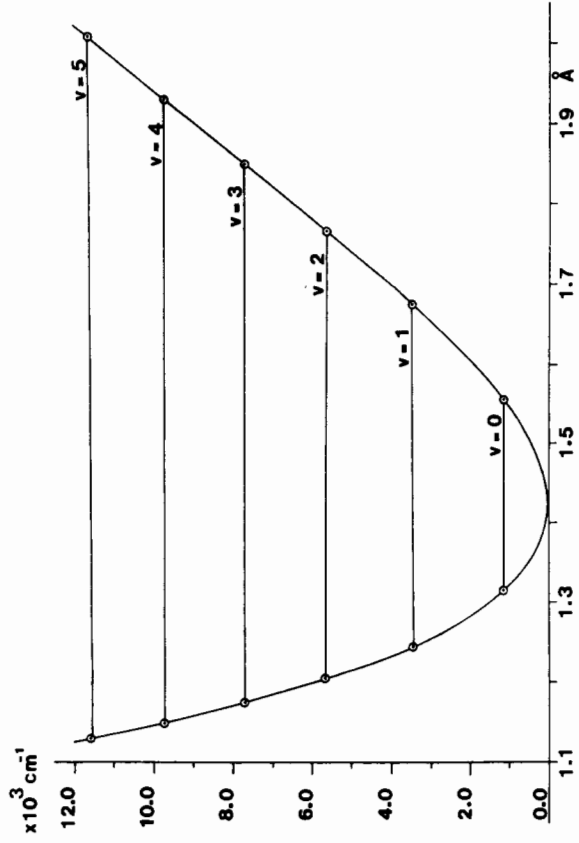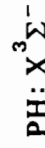
PH: X $^3\Sigma^-$

Figure 11   The RKR curve of the ground $X^3\Sigma^-$ state of PH (187). This curve was calculated from the vibration-rotation constants extracted from the infrared emission spectrum (Figure 9).

NONMETAL NITRIDES   Only two nonmetal nitrides, CN (238, 239) and PN (240), have known infrared vibration-rotation spectra. SiN has an infrared electronic transition, $A^2\Pi \to X^2\Sigma^+$ (241). CN was detected both by diode laser absorption spectroscopy (238) and Fourier transform emission spectroscopy (239). For the emission work, hot CN was made in carbon tube furnace (King furnace) with admitted nitrogen gas (239). PN has a $^1\Sigma^+$ ground state and is relatively long-lived (240). In fact, since PN can be made by heating P_3N_5 in a tube furnace (240), it could be classified as a high temperature molecule.

Triatomic Molecules

DIHYDRIDES   The most well-studied member of this family is NH_2, which has been extensively studied by numerous techniques (Table 8). The v_2 bending mode of NH_2 has been studied by CO and CO_2 laser magnetic resonance (243–245), diode laser spectroscopy (246), and, most recently, by Fourier transform absorption spectroscopy (248). The v_2 mode of ND_2 has been detected by infrared-optical double resonance with a CO_2 laser and a visible dye laser by Muenchhausen & Hills (247). For NH_2, the v_1 and v_3 modes were measured with a difference frequency laser spectrometer (246). Hills & McKellar detected the v_2 mode of PH_2 by laser magnetic resonance (249). The v_2 mode of SiH_2 was discovered by Yamada et al (242) by infrared diode laser kinetic spectroscopy. This work on SiH_2 completes the silane family, SiH, SiH_2, and SiH_3, of transient molecules. The silane family of molecules is important in the plasma deposition of Si from silanes in the semiconductor industry, and the observation of vibration-rotation spectra allows the development of infrared diagnostics.

MONOHYDRIDES   The HCO molecule has been extensively studied by many spectroscopic techniques ranging from laser electric resonance (LER) to Fourier transform absorption spectroscopy (Table 9). A similarly complete set of measurements is available for HO_2. Apart from the laser magnetic resonance spectrum of HSO, this list (Table 9) is padded with HBS, HBO, HNC, and HNO. These four molecules are rather long-lived species compared to the other molecules discussed in this review. In fact, HNC and HBS were recorded first at high resolution by Maki & Sams (251, 269) with a grating spectrometer, before the recent Fourier transform absorption spectra measurements (250, 270). The spectrum of HBO was recorded by diode laser spectroscopy with discharge modulation of a B_2H_6, O_2, and He mixture (268).

NONHYDRIDES   Table 10 displays the known vibration-rotation spectra of triatomic molecules that do not contain hydrogen. The FBS, ClBS, BrBS,

SiF_2, and NF_2 molecules could be classed as high temperature molecules because they can be readily produced in tube furnace reactions. FBS, ClBS, and BrBS were made by passing halogen disulfides X–S–S–X over heated boron (273). Similarly, SiF_2 (288) can be made by passing SiF_4 over heated Si, while NF_2 (289–293) is readily available from the thermolysis of N_2F_4. The NCO, FO_2, N_3, and FCO molecules are provided by F or Cl atom reactions such as $F + HNCO \to HF + NCO$ (281–283). Some relatively stable molecules such as BO_2, FBO, and ClBO are made readily in simple electrical discharges of mixtures of gases, for example discharging a mixture of BF_3 and O_2 diluted with He yields the closed-shell FBO molecule (271). Excimer laser photolysis of carbon suboxide, OCCCO, allowed Yamada et al (280) to detect the v_1 mode of CCO near 1970 cm^{-1} by diode laser kinetic spectroscopy.

Tetraatomic and Larger Molecules

As transient molecules become larger, recording their spectra becomes increasingly difficult. One reason for this difficulty is that as the rotational constants decrease (particularly for nonlinear, nonhydride molecules), the rotational partition function increases. This has a devastating effect on infrared absorption spectra because the population of a great many rotational levels greatly increases the spectral congestion and decreases the absorption strength of a particular rotational transition (21). Effectively, the overall infrared band strength is distributed into the increasingly numerous rotation-vibration lines as the size of the molecule increases. The solution to this problem is well known—rotational cooling in a free jet expansion—but the technical difficulties are formidable. The recent work by Heath et al on C_5 (138) and by the Rice group (169) on NH_2 is encouraging; the problems of short path length and weak absorption can be overcome.

Table 11 summarizes the known spectra of larger transient molecules. The inclusion of the long-lived HBNH and BH_2NH_2 molecules while excluding, for example, NCNC (302, 303) and CH_3CP (304), is particularly arbitrary. The experts in the area of semistable molecules, such as Kroto or the Winnewissers, need to review this area.

The elusive BH_3 molecule has finally been detected (294) by diode laser kinetic spectroscopy of diborane, B_2H_6, or BH_3CO. Discharge modulation spectroscopy of B_2H_6 in He also proved successful in making BH_3. Although CH_3 is planar (Table 4) and CF_3 (297) is pyramidal, the CH_2F molecule (296) displays some nonplanar tendencies (quasiplanar molecule). The NO_3 spectra are also unusual because of the presence of a low-lying $\tilde{A}^2E'$ state near the $\tilde{X}^2A_2'$ ground state (300, 301).

ACKNOWLEDGMENTS

Table 1 Infrared vibration-rotation spectra of metal hydrides

Molecule	Techniques	References
LiH, LiD	diode, FTS	73, 74
NaH	diode, FTS	75, 76
KH	diode	77
RbH	diode	78
CsH	diode	79
MgH, MgD	diode	80
CaH, CaD	diode	81
SrH	diode	82
BaH	diode	83
AlH	FTS	84
GaH	diode	85
InH	diode	86
TlH	diode	87
GeH	LMR	88
SnH	LMR	89
PbH	diode	307
AsH	diode	90
BiH, BiD	diode	91
SeH, ScD	LMR	92–94
TcH	FTS	95
CuH	FTS	96
AgH	diode	97
ZnH	diode	98
CdH	diode	98
NiH	LMR	99,
CoH	LMR	305
MnH	diode	100

Table 2 Vibration-rotation spectra of metal halides

Molecule	Techniques	References
LiF	diode	101
LiCl	FTS, diode	102, 103
LiBr	diode	104
LiI	diode	105
NaF	diode	106
NaCl	diode	107, 108
NaI	FTS	309
KF	diode	109
KI	FTS	309
RbF	FTS	110
CsF	FTS	110
AlF	diode	109
InF	FTS, diode	111
TlCl	FTS	112

Table 3 Vibration-rotation spectra of high temperature chalcogenides

Molecule	Techniques	References
SiO	diode, FTS	113, 114
GeO	diode	115
SnO	diode	116
PbO	diode	117
CS	grating, diode, FTS	118–122
SiS	FTS	‡
GeS	FTS, diode	123
PbS	diode	124
MgO	diode	125
CaO	diode	126, 127
SrO	diode	125
BaO	diode	128
LiO	diode	129

‡ C. Frum, P. F. Bernath, work in progress.

Table 4 Infrared vibration-rotation spectroscopy of pure carbon chain molecules and hydrocarbon free radicals

Molecule	Techniques	References
C_3	diode, FTS	133–135
C_5	diode, FTS	136–139
CH	difference freq., FTS	140–142
CH_2, CD_2	LMR, diode	143–148
CH_3, CD_3	difference freq., diode	149–153
CCH, CCD	diode, color center laser, FTS	34, 154–164
C_2H_3	diode	165
C_2H_5	diode	166

Table 5 Infrared vibration-rotation spectra of nonmetal hydrides

Molecule	Techniques	References
BH	FTS	174
CH	See Table 4	
SiH	diode, FTS, LMR	175–179
NH	difference freq., FTS, color center	42, 180–185
PH, PD	diode, FTS, LMR	186–188
OH, OD	color center, FTS, difference freq.	47, 48, 184, 189–194
SH, SD	difference freq., FTS, LMR	195–200

Table 6 Infrared vibration-rotation spectra of nonmetal halides

Molecule	Techniques	References
BF	diode	201, 202
BCl	diode	203
CF	LMR, diode	204, 205
CCl	FTS, diode	206, 207
SiF	diode	208
NF	diode	209
NCl	diode	210
PF	diode	211
PCl	diode	212
FO	diode, LMR, FTS	23, 213–216
ClO	LMR, diode, FTS	217–221
BrO	LMR, diode, FTS	222, 223, 308
SF	diode	224
SCl	diode	225, 226

Table 7 Infrared vibration-rotation spectra of nonmetal chalcogenides

Molecule	Techniques	References
CS, SiO, SiS	See Table 3	
NS	FTS, diode	227, 228
NSe	LMR	229
PO	diode	230
PS	diode	231
AsO	LMR	232
SO	FTS, difference freq., diode, LMR	233–236
SeO	LMR	237

Table 8 Infrared vibration-rotation spectra of nonmetal triatomic dihydride molecules

Molecule	Techniques	References
CH_2	See Table 4	
SiH_2	diode	242
NH_2, ND_2	LMR, difference freq., diode, IR-optical D.R., FTS	169, 243–248
PH_2	LMR	249

Table 9 Infrared vibration-rotation spectra of nonmetal triatomic monohydrides

Molecule	Techniques	References
HBO	diode	268
HBS, DBS	grating, FTS	269, 270
HNC	FTS, grating	250, 251
HCO, DCO	LER, diode, FTS, LMR, difference freq.	43, 57, 252–256
HNO	LER, FTS	257–259
HO_2, DO_2	diode, difference freq., LMR	260–266
HSO	LMR	267

Table 10 Infrared vibration-rotation spectra of triatomic nonhydrides

Molecule	Techniques	References
FBO	diode	271
ClBO	diode	272
FBS	FTS	273
ClBS	FTS	273
BrBS	FTS	273
FCO	diode	274
FO_2	diode, FTS	275, 276
BO_2	diode, FTS	277–279
CCO	diode	280
NCO	diode, LMR	281–283
NNN	FTS, LMR	29, 284
CF_2	diode, FTS	285–287
SiF_2	FTS	288
NF_2	diode, LMR	289–293

Table 11 Infrared vibration-rotation spectra of nonmetal molecules with four or more atoms

Molecule	Techniques	References
BH_3	diode	294
CH_3	See Table 4	
SiH_3	diode	295
CH_3F	diode	296
CF_3	diode	297
BH_2NH_2	FTS	298
HBNH	diode	299
NO_3	diode, FTS	300, 301

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