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HIGH-RESOLUTION SPECTROSCOPY USING TUNABLE DIODE LASERS: TECHNIQUES AND APPLICATIONS*

by

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Introduction

There are now about a dozen methods for generating tunable monochromatic infrared radiation. These are summarized in Table 1, together with indications of their wavelength coverage, resolution, and power levels. (It should be emphasized that resolution and output power depend upon details of construction and operation and may vary greatly with wavelength and operating conditions, so these entries are only approximate. The references have been chosen to give rapid access to the literature, and do not reflect priority of development; review articles have been cited where possible.)

Table 1. Generation of Tunable Monochromatic Infrared Radiation

Device	Wavelength coverage [μm]	Highest reported resolution [cm^{-1}]	Approximate power [W][a]	
			cw	pulsed
Semiconductor diode lasers[1-6]	0.4-34	2×10^{-6}	10^{-3} (0.1)	10 (10^2)
Gas lasers:				
High pressure CO_2 laser[2,5]	9-11	3×10^{-6}	1	10^3
Zeeman-tuned gas lasers[5,6]	3-9	3×10^{-3}	10^{-3}	
Raman scattering processes:				
Spin-flip Raman laser[2,3,5-9]	3.0			
	4.9-6.5	3×10^{-8}	1	10^3 (10^4)
	8.7-17	3×10^{-5}		10^2 (10^3)
	80-120	0.1		10^{-6}
Polariton laser[2,3]	16-20, 40-710	0.5		10 (10^3)
Tunable-laser-pumped Raman scattering[2]	0.8-15	0.3		10^3 (10^8)
Optical parametric oscillators[2,3,5,10]	0.4-17	1×10^{-3}	10^{-3}	10^2 (10^6)
Non-linear optical mixing techniques:				
Difference frequency generation[2,5,6,11]	1.1-25, 52-2000	3×10^{-6}	10^{-6} (10^{-3})	(10^4)
Two-photon mixing (microwave modulation)[5,12]	9-11	3×10^{-5}	$\sim 10^{-6}$	
Four-photon mixing[2,5,6]	2-31	0.1		~ 0.1
Coherent Raman mixing[13]	3.3-70			
Miscellaneous lasers:				
Color center laser[14]	0.9-3.3	~ 0.03	5×10^{-3}	
Free electron laser[15]	3.4	7		10^4

[a] Typical and (maximum).

While high-resolution spectroscopy has been performed with the majority of these devices, tunable semiconductor diode lasers (SDL's) have proved to be most convenient. Perhaps 75% of the infrared laser spectra reported to date have been obtained with diodes, and this proportion will doubtless increase now that complete SDL spectrometers are available commercially.

Techniques of Tunable Diode Laser Spectroscopy

The system in use at Los Alamos is illustrated in Fig. 1. The diode is mounted at the center of a superconducting magnet contained in a liquid helium cryostat. This allows us to take advantage of

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the increased tuning range provided by small magnetic fields (<7 kG) as described by Flicker and Nereson.[16] Once the desired mode has been obtained, the SDL is current tuned by the output of a ramp generator.

The laser emission is collected by an f/3 ZnSe lens and focused on the entrance slit of a Spex 1-m monochromator, which is used to select a single laser mode and to provide a coarse frequency calibration. A 700-Hz mechanical chopper immediately in front of the entrance slit modulates the beam for detection by a lock-in amplifier. At the exit slit of the monochromator the beam is collimated by a second ZnSe lens and then divided by a germanium beamsplitter into sample and calibration beams; each of these is focused by a parabolic mirror onto a Cu-doped germanium detector. The sample and calibration signals are recorded simultaneously on a two-pen XYY' recorder, with the current ramp driving the X axis.

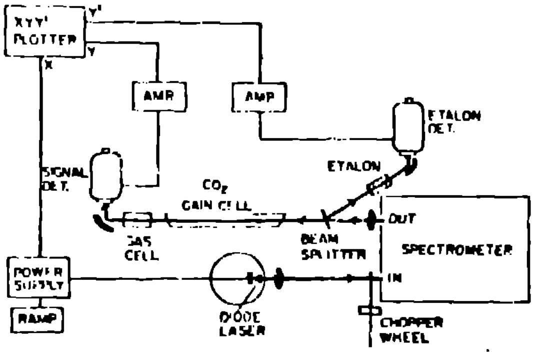

Fig. 1. Experimental arrangement for SDL spectroscopy.

Relative frequency calibration (i.e., calibration of tuning rate) is provided by interference fringes from a germanium etalon; the fringe spacing of such an etalon at normal incidence is

$$\Delta\nu = 1/2h[n - \lambda(dn/d\lambda)],$$

where h is the etalon length and n is the index of refraction of germanium at the wavelength λ of measurement. The best current values of n and dn/dλ are probably those of Herzberger and Salzberg,[17] but a new and more accurate determination of these quantities would be desirable. There are certain difficulties associated with the use of germanium etalons: for example, small changes in the angle of incidence of the SDL beam on the etalon, such as can be expected if a non-scanning monochromator is used for mode selection, can affect the fringe spacing.[18] We now insure that during each spectral scan the monochromator grating drive is advanced at a rate that keeps the image of the diode motionless at the exit slit. With suitable care, etalons can provide relative frequencies accurate to 0.001 cm^{-1} or better; to improve much upon this it will probably be necessary to use heterodyne methods, which require a more sophisticated level of instrumentation.

Absolute frequency calibration is something of a problem in tunable laser spectroscopy. Throughout most of the infrared the only available standards are absorption lines of simple molecules. The IUPAC tabulation[19] is the best source of such data, and it lists line frequencies with an absolute accuracy of from 0.005 to 0.0002 cm^{-1}, depending on the molecule, over the region 1 to [illegible]350 cm^{-1}. These lines are meant for users of grating spectrometers, however, and are often not spaced as closely as would be desirable for laser spectroscopy. Recently Knoll et al.[20] have used SDL's to compare the accuracy of CO_2 and HCN lines in the 14- to 15-μm region and found that they agree to within ±0.0008 cm^{-1}; doubtless there will be further attempts to check and improve the accuracy of molecular absorption standards in the near future.

In the 9-11 μm region, very accurate absolute frequency standards can be established from the CO_2 spectrum. A convenient arrangement is to place a high-voltage CO_2 gain cell in the sample beam, as shown in Fig. 1. This gives a strong increase in signal at the positions of the CO_2 laser frequencies, which are known with a precision of about 30 kHz (10^{-6} cm^{-1}).[21] Unfortunately, these lines are spaced by 1.8 cm^{-1} which limits their usefulness. Additional higher-level CO_2 laser bands have been reported by Reid and Siemsen,[22] and these may help to fill the gaps between the principal laser transitions. Many such emission lines have recently been observed at Los Alamos using a gain cell, and accurate measurements of their frequencies are in progress.[23]

These various calibration techniques are illustrated in Fig. 2, which shows a portion of the spectrum of $^{192}OsO_4$, with the tuning rate calibrated by a 3-in (7.544-cm) etalon. The upper trace shows the output of the sample beam in a separate scan in which the OsO_4 cell was replaced by a CO_2 gain cell and a low-pressure ammonia absorption cell, in series. The absorption lines of NH_3 and the P(14) gain line of CO_2 at 949.479 313 cm^{-1} provide absolute frequency markers.

Spectra of Some Molecules Important in Laser Chemistry

We will restrict the present discussion to SF_6 and OsO_4, two molecules that are strong absorbers of CO_2 laser radiation in the 10.5-μm region. Since the discovery of isotopically-selective dissociation in SF_6 in 1975, the literature on this subject has grown rapidly. Table 2 summarizes references to laser-induced photodissociation and laser isotope separation (LIS) in SF_6 and OsO_4 through early 1977. This work, together with the observation of a wide variety of non-linear optical phenomena in both molecules (for references, see [56]), has stimulated an interest in identifying the exact molecular transitions that are in resonance with the various laser frequencies. This has recently been accomplished with SDL spectra.

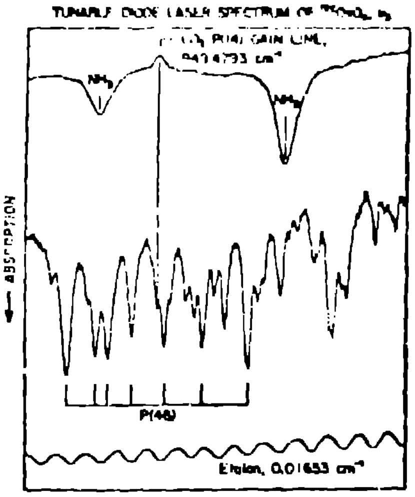

Fig. 2. The P(46) manifold in ν_3 of $^{192}OsO_4$, recorded with calibration lines and etalon.

Both SF_6 and OsO_4 are highly symmetric, with equilibrium molecular symmetries O_h (octahedral) and T_d (tetrahedral), respectively. Such molecules exhibit a complex splitting of the individual rotational manifolds due to tensor perturbations. The theory of this band structure was developed in the early 1960's by Moret-Bailly[57] and Hecht[58] and was applied to the infrared absorption spectra of methane and its analogues. Their results for the frequencies of transitions in the P, Q, and R branches can be written[59]

Table 2. Photodissociation and LIS Experiments on SF_6 and OsO_4.

Mol.	Topic	Reference
SF_6	isotope separation	Ambartsumyan et al.[24]
	isotope separation	Lyman et al.[25]
	comparison of SF_6 with BCl_3, CF_2Cl_2, SiF_4; theory	Lyman & Rockwood[26]
	theory (dissociative electron attachment)	Allen et al.[27]
	isotope separation as function of pressure, intensity	Ambartsumyan et al.[28]
	dissociation by pumping combination bands	Ambartsumyan et al.[29]
	theory	Bloembergen[30]
	review article	Letokhov & Moore[31]
	isotope separation as function of pressure and laser parameters	Hancock et al.[32]
	dissociation as function of frequency, power; theory	Ambartsumyan et al.[33]
	study of dissociation and enrichment; theory	Ambartsumyan et al.[34]
	dissociation by two-frequency pumping	Ambartsumyan et al.[35]
	theory (anharmonic oscillator)	Mukamel & Jortner[36]
	isotope separation	Dupré et al.[37]
	theory (excitation to quasi-continuum)	Larsen & Bloembergen[38]
	threshold intensity for dissociation	Keefer et al.[39]
	dissociation by two-frequency pumping	Ambartsumyan et al.[40]
	theory (anharmonic splitting of excited vibrational states)	Cantrell & Galbraith[41]
	saturation	Bagratashvili et al.[42]
	theory	Mukamel & Jortner[43]
	energy dependence of dissociation	Campbell et al.[44]
	isotope separation as function of laser parameters	Gower & Billman[45]
	theory	Stone et al.[46]
	dissociation in a molecular beam	Coggiola et al.[47]
	dissociation by short pulses	Kolodner et al.[48]
	dissociation as function of energy and pressure, theory	Fuss & Cotter[49]
	theory (anharmonic splitting of excited vibrational states)	Jensen et al.[50]
	dissociation rate	Tal et al.[51]
	effect of mode locking on reaction yield & isotopic selectivity	Lyman et al.[52]
	dissociation thermodynamics	Black et al.[53]
OsO_4	isotope separation	Ambartsumyan et al.[54]
	dissociation rate as a function of frequency	Ambartsumyan et al.[55]
	dissociation by two-frequency pumping	Ambartsumyan et al.[79]
	dissociation by two-frequency pumping	Ambartsumyan et al.[80]

$$\nu_{P,R}(J,p) = m + nM + pM^2 + qM^3 + (g - hM + kM^2)\bar{F}(4) \tag{1}$$

$$\nu_Q(J,p) = m + vJ(J+1) + wJ^2(J+1)^2 + [-2g + uJ(J+1)]\bar{F}(4) \tag{2}$$

in dominant approximation, with off-diagonal terms in the Hamiltonian neglected. Here J is the total angular momentum quantum number, $M = [-J,(J+1)]$ for [P,R]-branch transitions, p designates the sublevel (classified according to its tetrahedral or octahedral symmetry), and $\bar{F}(4)$ is the product of a symmetry-adapted fourth-rank tensor operator times a J-dependent factor. The first terms in these equations are the usual scalar expressions for the manifold frequencies, where m is the band origin, $n = B_v+B_0+2(B\zeta)_i$, $p = v = B_v-B_0$, etc.; the second or tensor portion describes the splitting of the individual J-manifolds into their various symmetry-allowed component levels. $\bar{F}(4)$ will be different for a given component in each of the three branches; values of $\bar{F}(4)$ have recently been tabulated for all (J,p) levels up to J = 100 by Krohn.[60]

For methane-type molecules, with small moments of inertia, observed transitions are pretty much limited to J < 15. There was no need to consider larger angular momentum states because the bands of heavier molecules that exhibit high-J transitions simply could not be adequately resolved before the development of tunable laser spectroscopy. As an example of the data that we deal with now, Fig. 3 illustrates a portion of the P branch of the bending fundamental ν_4 of CF_4, showing the manifold P(54) split into well-resolved tetrahedral components.

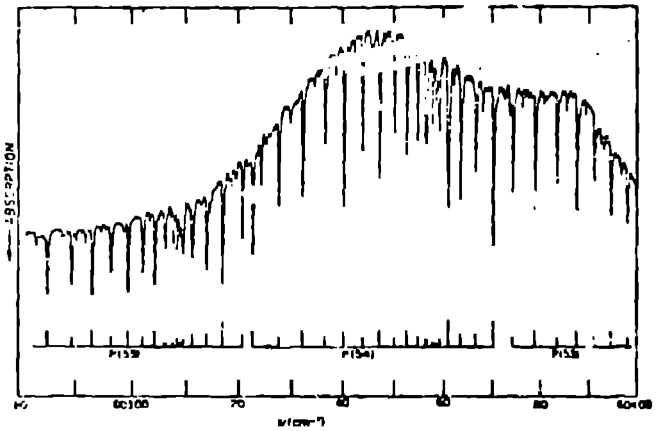

Fig. 3. Spectrum of CF_4 between 602.8 and 604.0 cm^{-1}, showing resolved high-J P-branch manifolds.

Sulfur Hexafluoride

In 1970 Hinkley[61,62] used SDL's to obtain Doppler-limited spectra of the ν_3 band (infrared-active stretching fundamental) of SF_6 in the regions within ±1 GHz of the CO_2 P(14)-P(24) laser lines. These revealed a complex vibration-rotation structure in which the individual manifolds such as that shown in Fig. 3 were badly overlapped. Because of the small fraction (~2%) of the band covered in these measurements, it was not possible to assign the individual transitions. In 1975 Aldridge et al.[63] first obtained at Los Alamos SDL spectra that were nearly continuous over much of the ν_3 fundamental. In conjunction with this experimental work, Cantrell and Galbraith[64] derived the correct nuclear-spin statistical weights for octahedral XY_6 molecules, which are 2,10,8,6,6 for sublevels of p = A_1,A_2,E,F_1,F_2 symmetry if the Y-nuclei have spins I = 1/2. These advances allowed much of the rotational structure to be assigned. The first step[65] was to assign Hinkley's spectra near the CO_2 P(14), P(18), and P(20) lines, which fall in the P and R branches at moderate values of J [approximately R(28), P(32), and P(59), respectively]. Next the region of CO_2 P(16), which lies in the dense Q branch of SF_6, was successfully assigned,[66] and recently the high-J regions at CO_2 P(12) and P(22) have been identified.[67] In this last step it was necessary to consider transitions having J as high as 95.

The complexity of these spectra can be appreciated by reference to Fig. 4, which shows a 0.09-cm^{-1}-wide portion of the SF_6 ν_3 Q branch centered at CO_2 P(16) (947.741 978 cm^{-1}). All of these lines are identified in the figure; some of the transitions are grouped into sub-branches which are identified as Q_A,Q_B,...,Q_7. We won't go into the nature of the Q-branch structure here, but refer instead to the original paper[66] for the meaning of this nomenclature.

Some 10,000 transitions have thus been identified between 942 and 952 cm^{-1}. With these detailed assignments available, we could identify the absorptions in some very-high-resolution saturation spectra recently obtained by Clairon and Henry,[68] within the gain profiles of the various CO_2 laser lines, and measured with an accuracy of ±30 kHz (10^{-6} cm^{-1}) in absolute frequency. A total of 15 lines (2 in the P branch, 9 in the Q branch, and 4 in the R branch) were so measured[58] and have been used to determine the spectroscopic constants of this band to high precision.[69] For this analysis it was necessary to include the off-diagonal terms that were neglected in Eqs. (1) and (2); these corrections were made by an iterative procedure, and the final values of the parameters were determined as follows (in cm^{-1}):

Scalar constants: $m = 947.976\ 575\ 9 \pm 0.000\ 004\ 3$
$n = 0.055\ 817\ 60 \pm 0.000\ 000\ 14$
$p = (-1.618\ 642 \pm 0.000\ 022) \times 10^{-4}$
$v = (-6.998\ 70 \pm 0.000\ 18) \times 10^{-5}$
$q = (1.0389 \pm 0.0038) \times 10^{-8}$

Tensor constants: $g = (-2.458\ 283 \pm 0.000\ 082) \times 10^{-5}$
$h = (-5.63 \pm 0.12) \times 10^{-10}$

The standard deviation for 15 lines was 0.14 MHz = 4.7 × 10^{-6} cm^{-1}. Note that the precision in the band origin, m, is ± 4.5 parts in 10^9, or about that of the currently-accepted value of the velocity of light! Such results were beyond the reach of infrared methods until the development of laser spectroscopy.

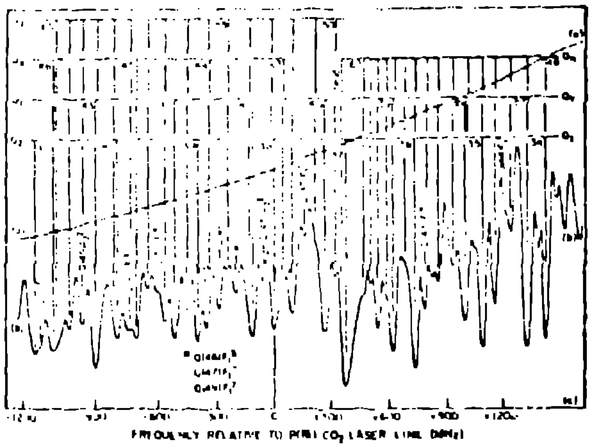

Fig. 4. Detail of SF_6 Q-branch absorption between 947.70 and 947.80 cm^{-1}. The SF_6 pressure was (a) 0 torr; (b) 0.1 torr; trace (c) is the zero.

The SF_6 assignments near the CO_2 P(12) to P(22) laser lines are given in Table 3. This table also includes a summary of pulse breakup as observed in self-induced transparency (SIT).[70-72] The immediate application of these results to the non-linear optics experiments can be summarized as follows:

(1) The disputed question of whether near-ideal pulse breakup in SIT can occur on a degenerate transition (see the references cited by Gibbs et al.[73]) is clearly answered in the affirmative by the results at CO_2 P(12). Table 3 suggests that pulse reshaping can be observed on any P- or R-branch SF_6 transition not accompanied by significant hot-band absorption, and thus supports the conclusion of Gibbs et al.[73] that breakup requires only a non-overlapping P or R transition, not necessarily a non-degenerate one.

(2) The hypothesis of appreciable overlap of P and Q transitions at CO_2 P(18)-P(22), and of R and Q transitions at CO_2 P(14), suggested by Heer and Nordstrom[74] to account for their photon echo polarization measurements, can definitely be rejected.

Table 3. Summary of Assignments and Observed SIT Pulse Breakup in SF_6.

CO_2 line	Nearest ground-state SF_6 transition	Detuning [MHz][68]	SIT results		Peak strength [$cm^{-1}torr^{-1}$]	Adjacent hot-band absorption [$cm^{-1}torr^{-1}$]
			T [K]	Observed pulse breakup		
P(12)	R(66) $A_2^0+F_2^0+F_1^0+A_1^0$	-23.02	300	Near ideal[70]	0.50	~0.03
P(14)	R(28) A_2^0	+17.59	300	Near ideal[70]	0.44	0.14
P(16)	Q(38) $F_1^0+E^0+F_2^0$	-7.24	300	Poor[70]	0.85	0.23
P(18)	P(33) A_2^1	+6.71	300	Extremely poor[71]	0.42	0.32
			195	Appreciable[72]	2.75	0.14
P(20)	P(59) A_2^3	+27.76	300	None[70,71]	0.25	0.25
P(22)	P(84) $A_2^1+F_2^3+F_1^3+A_1^1$	~+50	300	...	0.19	0.23

A precise value for the isotope shift in ν_3 of SF_6 is of interest in some of the isotope separation experiments (Table 2). We have resolved the Q branch of $^{33}SF_6$ present in its natural abundance (0.76%) and have performed an analysis similar to that of $^{32}SF_6$.[66] The ^{32}S-^{33}S shift is 8.970 ± 0.003 cm^{-1}. Similar measurements will be made on $^{34}SF_6$, and will allow a refinement of the general quadratic valence force field of SF_6.[75]

Osmium Tetroxide

The stretching fundamental ν_3 of OsO_4 at 961 cm^{-1} shows well-resolved PQR structure when recorded with a grating spectrometer,[76] but individual rotational transitions have not been resolved except by saturation spectroscopy within the Doppler widths of the CO_2 laser line.[77,78] Because there are seven stable isotopes of osmium, the use of isotopically pure material is necessary to disentangle the rotational fine structure. Kompanets et al.[78] recognized this problem and recorded saturation spectra of the ^{187}Os, ^{189}Os, ^{190}Os, and ^{192}Os species separately, but these studies of narrow spectral regions were not adequate for line assignments to be made.

Recently we have recorded at Los Alamos all of the ν_3 band of $^{192}OsO_4$ (isotopic purity 99.06%) with a Nicolet Fourier transform spectrometer (resolution 0.05 cm^{-1}), and have investigated selected portions of this band in more detail with SDL's. The P(46) manifold is shown in Fig. 2; note that it consists of just seven lines, of which one (the lowest-frequency, or leftmost, one in Fig. 2) contains two components-- a total of eight transitions. In contrast, a J = 46 manifold of SF_6, CH_4, or CF_4 contains 39 transitions that group themselves into about 15 resolvable lines (cf. P(54) of CF_4 in Fig. 3). The reason for the difference is that oxygen-16 has zero nuclear spin, and as a result only rotational levels of A symmetry exist. Since, on the average, only about 20% of spherical-top rotational levels have A_1 or A_2 symmetry, a considerable simplification of the spectrum results for tetroxide molecules. Note also the large number of unassigned hot-band transitions in Fig. 2; at 300 K (at which this spectrum was recorded), 69% of the OsO_4 molecules are excited to vibrational states above the ground state, resulting in a strong and complex hot-band background. We have since obtained spectra of OsO_4 cooled to 245 K (ground-state population 46%), which significantly reduces the interference due to hot-band lines.

The analysis of this band is still in progress, but we have assigned the P and R branches and now have firm assignments throughout most of the Q branch. *Preliminary* values for the $^{192}OsO_4$ ν_3 constants are (in cm^{-1}):

Scalar constants: $m = 960.703 \pm 0.005$
$n = 0.2363 \pm 0.0003$
$p = (-1.74 \pm 0.05) \times 10^{-4}$
$v = (-1.4 \pm 0.1) \times 10^{-3}$

Tensor constant: $g = (1.12 \pm 0.02) \times 10^{-5}$

The strongest absorption observed by Kompanets et al.[78] in $^{192}OsO_4$ was at about +1.5 MHz from CO_2 P(14). They assumed that this was a ground-state transition with J = 45, and measured its saturation and pressure-broadening characteristics. Our measurements (Fig. 2) indicate that this absorption originates from a hot-band transition; the nearest ground-state transition is the P(46) line at 949.484 cm^{-1}, or at about +150 MHz from CO_2 P(14), well outside the region covered by the saturation spectra.[78] Because of the sparseness of lines in the OsO_4 spectrum compared with that of, say, SF_6, it may be that none of the lines observed inside the gain profiles of the CO_2 laser emission is a transition from the vibrational ground state. Further work on this molecule, including intensity measurements (from which the transition moment can be estimated) and spectra of other isotopic species, is in progress.

Acknowledgements

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