THE SPECTROSCOPIC DETECTION OF MOLECULAR SPECIES USING A SCANNING NARROW-BAND DYE LASER

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Summary

A continuously scanning, frequency doubled, tunable dye laser, pumped by a pulsed nitrogen laser, has been used to excite fluorescence of gaseous molecules. It was possible not only to scan continuously the fundamental wavelength, but also to scan the excitation wavelength when frequency doubled (270 - 325 nm) over a range exceeding 2 nm with a bandwidth of less than 0.01 nm.

Insertion of an etalon into the dye laser cavity resulted in a narrowing of the laser output bandwidth to <0.002 nm in the fundamental and to 0.0005 nm in the ultraviolet (frequency-doubled) output. A simple technique has been devised for making almost linear, continuous scans of the narrow-band excitation wavelength over a range of 0.15 nm in the fundamental, or 0.08 nm in the second harmonic.

The results are exemplified by studies of the laser-induced fluorescence of I_2, SO_2 and the OH free radical. However, laser induced fluorescence from the atmospherically-important ClO radical could not be detected under similar conditions, and possible reasons for this result are discussed.

Introduction

The potential of laser-induced fluorescence as a sensitive and specific technique for the detection of gaseous molecules, including free radicals, is well-known [1, 2]. It is also an excellent method for the determination of energy transfer in elementary chemical reactions, as shown, for example, by Zare's pioneering work, in which the scattered products of the interaction of two molecular beams were investigated by laser-induced fluorescence [2]. Because a narrow-band laser (e.g. an argon ion laser) can excite only one vibrational level (and sometimes only one rotational level) in an electronically-excited state by single photon absorption,

laser-induced fluorescence can be used to greatly simplify observations of molecular spectra. This has been demonstrated in several studies of the I_2 molecule, which have been directed towards the measurement of the spectroscopic constants, including the hyperfine splitting constants, of this molecule [3].

Tunable dye lasers pumped by pulsed nitrogen lasers, flash lamps, or continuous-wave Ar ion lasers, offer the possibility of tuning the laser excitation wavelength to coincide with a known transition of a molecule. Dye lasers thus greatly extend the scope of laser-induced fluorescence. The peak power within the pulse emitted from a conventional pulsed dye laser can be sufficiently high to allow reasonably efficient (~ 5 - 15%) second-harmonic generation (frequency-doubling). Thus, with frequency-doubling, as in the present work using a N_2-pumped dye laser, useful laser output (1 - 500 μJ per pulse or more) from 700 nm down to 260 nm can be obtained with a range of dyes.

For quantitative spectroscopic work, or merely for the survey of fluorescence spectra, it is advantageous to be able to scan the laser excitation wavelength continuously, preferably linearly, with time. Some commercial dye lasers, such as the Molectron which incorporates a grating for wavelength tuning, may be scanned linearly with time in the fundamental. We have modified such a laser to also scan linearly in the ultraviolet (frequency-doubled output); with this system, two scans sufficed to record the entire excitation spectrum of the 1,0 band of the $A^2\Sigma^+ - X^2\Pi$ transition of OH, with a laser bandwidth of ~ 0.008 nm. Linear scanning of the laser excitation wavelength in the narrow bandwidth mode (*i.e.* ~ 0.002 nm in the fundamental, < 0.001 nm in the ultraviolet) was more difficult to achieve, because of the need to synchronously rotate the grating and the intracavity etalon at the correct relative rates. Development of a simple scanning technique in the narrow bandwidth mode is potentially valuable, because of the much greater precision available by wavelength tuning with an etalon as compared to a grating. Therefore, high resolution photoelectrically-recorded spectra, which are of low precision when based only on grating rotation, should be much superior with additional etalon rotation using the laser excitation technique. We exemplify this technique by reference to a part of the visible spectrum of I_2 and to the Q_2 and R_1 band heads of the 1,0 band of OH $A^2\Sigma^+ - X^2\Pi$.

Experimental

A tunable dye laser, pumped by a pulsed nitrogen laser, has been used to study fluorescence spectra of gaseous molecules (I_2, SO_2) and of the OH free radical, produced in a low-pressure flow system.
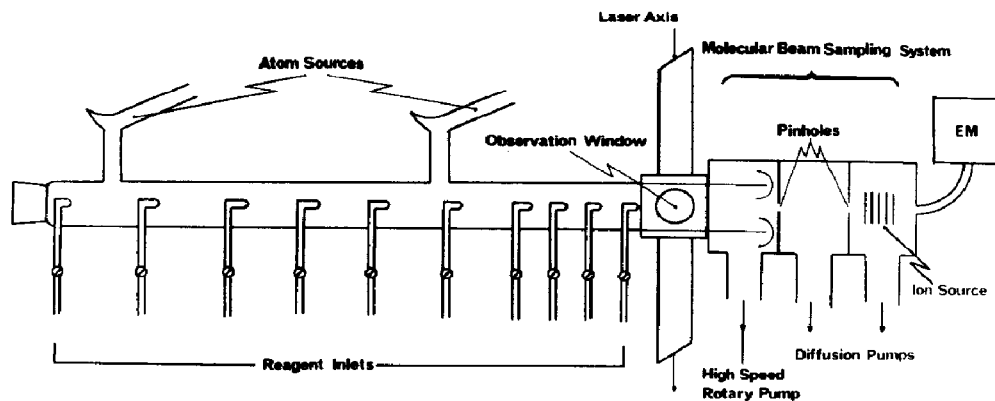
Fig. 1. Schematic diagram of the flow tube, optical cell and ancillary mass spectrometer.

The flow system

The flow system, Figure 1, comprised a Pyrex tube (900 mm long × 28 mm id) with 10 fixed reagent inlets, for kinetic studies on transient species (*e.g.* OH), and two side arms for atom production by microwave radiation. The flow passed through an optical cell which was constructed from brass, treated with a black nickel plate, and overcoated with teflon. The whole flow system was coated with Teflon so as to present a uniform and inert surface to reactive gases. The windows (silica) on the laser axis were heat sealed (onto long quartz side arms), cut at the Brewster angle. It was found to be necessary to seal the windows in this way as commonly used adhesives fluoresced brightly under u.v. laser radiation. The flow system was linked *via* a molecular beam sampling system to the ion source of a 90° magnetic mass spectrometer, in order to permit continuous analysis of free radicals and stable molecules. The system was pumped by a high speed rotary pump which gave typical flow velocities of 20 m s^{-1} at a flow tube pressure of 130 N m^{-2}.

Laser system

An outline of the laser detection system is shown in Figure 2. A pulsed nitrogen laser (Molectron UV 300), optically pumped a circulating dye solution with ~300 kW peak power per pulse of 10 - 15 ns duration at a repetition rate of 10 Hz. Addition of helium to the nitrogen flow greatly reduced the shot-to-shot intensity fluctuations, to less than ±10%. The dye laser (Molectron DL 400) is based on the design of Hänsch [4] and had a conversion efficiency of the order of 5 - 10%. The beam was steered *via* mirrors to the flow tube and focused into the centre of the flow tube by a concave mirror of 1 m focal length. The total fluorescence was collected, at right angles to the laser beam, with a photomultiplier cell (E.M.I. 6256 SA). Cut-off filters were used to block light at the laser wavelength, and when the emitted fluorescence was in the ultraviolet spectrum, another filter was used to block visible light. The output from
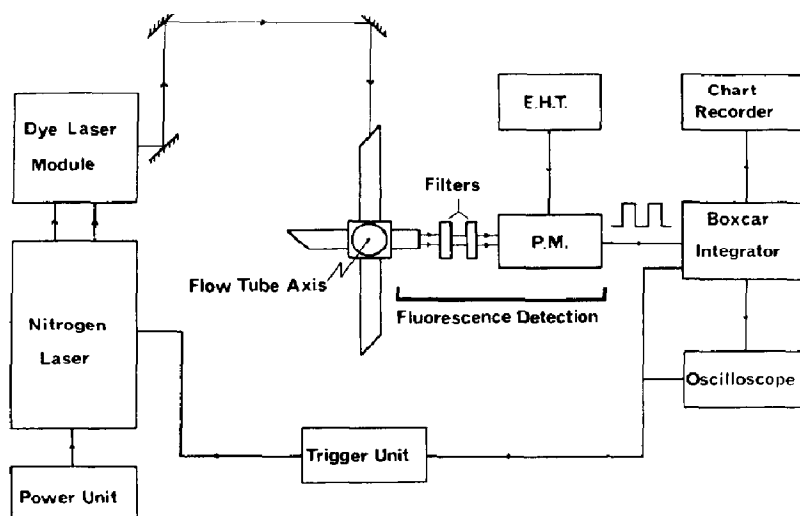
Fig. 2. Block diagram of the system for observing laser-induced fluorescence in a discharge flow system.

the photomultiplier was then processed through a boxcar integrator (PAR model 160) and onto a chart recorder. Alternatively, or simultaneously, waveforms of laser or fluorescence pulses were output directly onto a rapid oscilloscope (Tektronix 465).

The dye laser module

A range of dyes can be used to cover the wavelength range from about 340 to 760 nm, although the present studies were carried out in the wavelength range $520 \leqslant \lambda \leqslant 640$ nm. Four ethanolic dye solutions sufficed to cover this wavelength range: Rhodamine B ($597 \leqslant \lambda \leqslant 636$ nm), Rhodamine 6G ($571 \leqslant \lambda \leqslant 607$ nm), a mixture of Rh 6G + Na fluorescein ($540 \leqslant \lambda \leqslant 575$ nm), and Pilot 495 ($518 \leqslant \lambda \leqslant 583$ nm). The last mentioned dye, a proprietary coumarin (N.E.N. Chemicals Inc.) was particularly valuable in possessing a broad wavelength tuning range and a high output power. Wavelength tuning was by means of an echelle grating which terminates one end of the laser cavity. The other end was terminated by a mirror of 4% reflectivity and, using an intracavity beam expanding telescope (Fig. 3), a bandwidth of 0.01 - 0.02 nm was obtained. Continuous scans, at this bandwidth, of the fundamental beam are possible over the total range of each dye simply using a variable speed motor which was connected to the grating sine drive assembly.

Extracavity frequency doubling of the fundamental laser beam was achieved using crystals of potassium dihydrogen phosphate (KDP). These negative uniaxial crystals have a sufficiently large birefringence that the ordinary wave at the fundamental frequency can have the same propagation constant within the crystal as the extraordinary wave at twice the frequency, but obviously only for a unique direction of propagation of
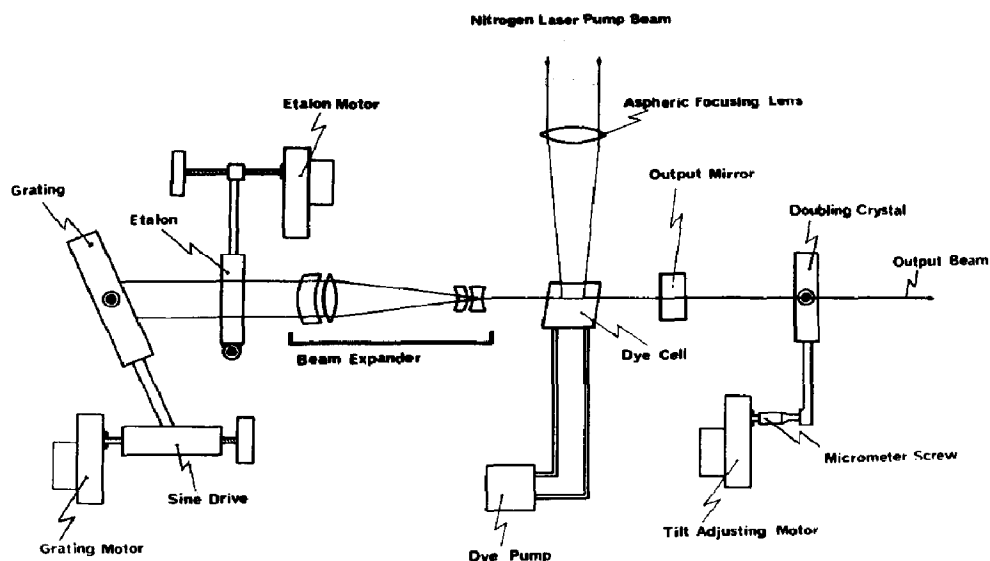
Fig. 3. Schematic diagram of the dye laser module.

radiation with respect to the principal optic axis. To maintain correct
phase matching of the fundamental and the harmonic radiation at different
wavelengths, the orientation of the crystal relative to the direction of
propagation of the fundamental beam must be varied. If exact phase
matching is lost, the efficiency of conversion, and hence the intensity of
the ultraviolet beam, falls. Equally important, parallelism of the directions
of incident and transmitted light leaving the crystal is lost. To enable
scanning of the ultraviolet wavelength, whilst maintaining exact phase
matching, a linear drive system comprised of a micrometer screw driven
by a variable speed stepping motor through a reduction gearbox (5000 : 1)
was constructed. As discussed below, a linear drive of the micrometer
controlling the crystal tilt was adequate. Five KDP crystals set in a carousel
at different orientations (Molectron DL 070) were used to provide a
tuning range from 259 to 318 nm. Figure 4 shows how the micrometer
setting (proportional to the tangent of the crystal tilt angle) had to be
varied to maintain exact phase matching when the wavelength is changed
as determined experimentally. (This crystal (No. 3) was used for the
study of the OH radical presented later). It can be seen that although this
plot is not linear, short sections, 5 nm in the fundamental, can be assumed
to be linear with negligible error. Thus continuous scans up to 2.5 nm in
the ultraviolet are possible, whereas the maximum scan range (at 300 nm)
without the doubling crystal drive is 0.2 nm. The phenomenon of
frequency doubling also caused a narrowing of the beam bandwidth from
0.015 nm to 0.005 nm, i.e. somewhat more reduction than would be
expected on a simple halving of the wavelength. The linear doubling
crystal drive used here was not capable of maintaining exact phase-matching
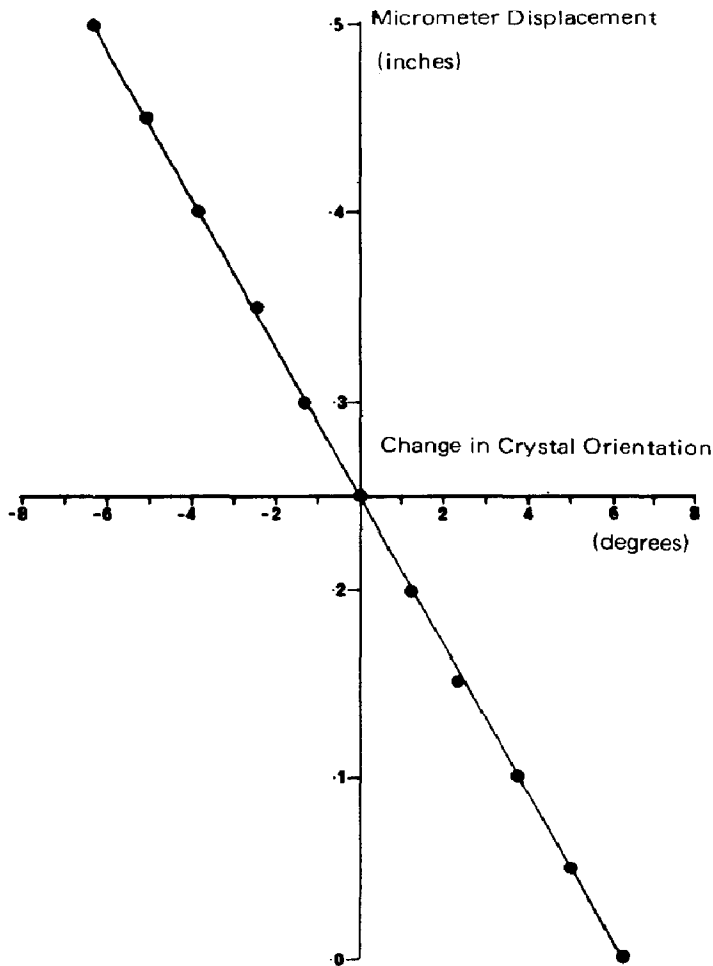over the very wide wavelength range (>10 nm) which has been reported

Fig. 4. (a) Plot showing the relative angle of the KDP crystal to the incident laser beam for the range of micrometer settings.

recently for a servo-controlled system [5] developed for the same purpose in a dye laser cavity employing (non-linear) prism tuning. On the other hand, the extreme simplicity and linear wavelength rate of the present system are most advantageous.

Narrowing of the fundamental laser bandwidth was effected by inserting a solid quartz Fabry-Perot etalon into the dye laser cavity between the beam expander and the grating, Figure 3. This etalon had a thickness of 3.011 mm, a free spectral range of 1.1 cm^{-1} and a finesse of 20 - 30; and it produced a bandwidth of about 0.001 nm in the fundamental. Wavelength tuning is carried out by simultaneously tilting the etalon and the grating about the correct orthogonal axes. It is a difficult problem to maintain synchronisation of the etalon and the grating when scanning. As the etalon is rotated through an angle dθ, the wavelength changes for a given order according to equation (1),
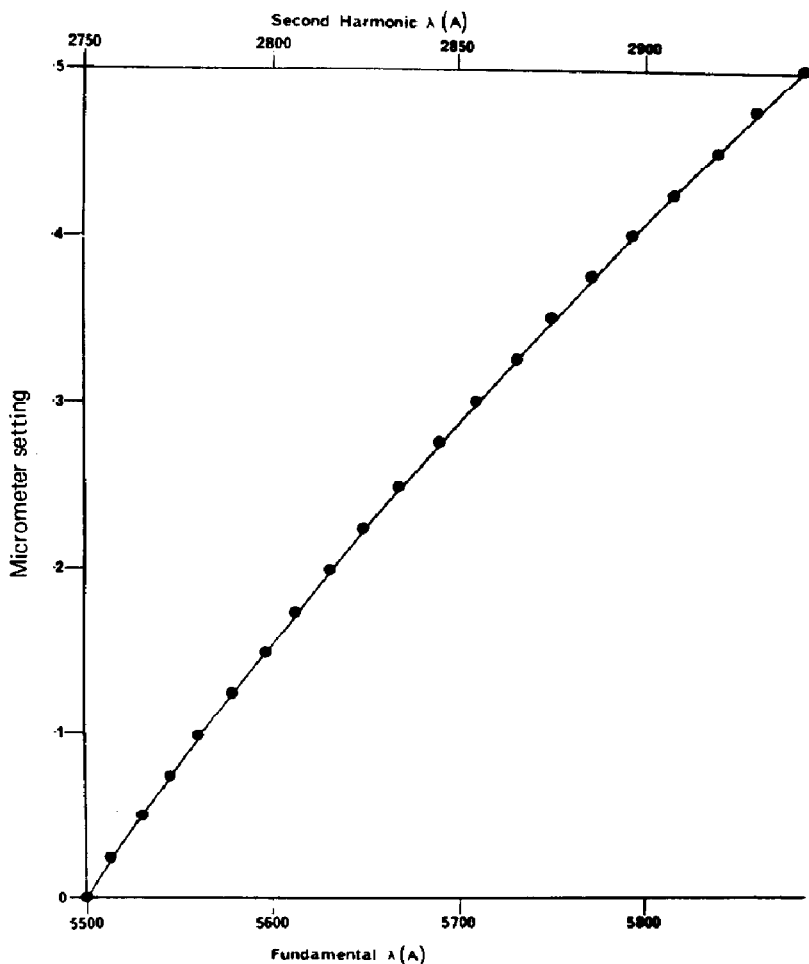
Fig. 4. (b) Plot of micrometer setting *versus* wavelength for correct phase matching in one of the crystals.

$$d\lambda = -\lambda_0\theta\,.d\theta\,/2n.n_d \tag{1}$$

where n is the refractive index of quartz at wavelength λ_0, θ is the angle of rotation from normal and λ_0 is the laser wavelength at $\theta = 0$. The dispersive index of quartz, n_d, at wavelength λ is given by,

$$n_d = n - \lambda_0 \frac{dn}{d\lambda}\bigg|_{\lambda_0}$$

Thus, the factor linking the grating scan rate to the etalon scan rate must include the refractive and dispersive indices of quartz. Since these are slightly both wavelength dependent, there is no simple linear relation of scanning rates which will hold for a long scanning range. When $d\theta/dt$ is linear, as with a simple drive, the best approximation to a linear $d\lambda/dt$ is obtained using as high θ values as are compatible with losses in the etalon.

We found that a reasonably constant $d\lambda/dt$, and close synchronisation of grating to etalon drive rates could be obtained by scanning linearly between the 8th and 11th etalon orders away from the normal ($\theta = 0°$, order ~15300 at 580 nm). Scanning, with the grating motor rate equal to one tenth of the etalon motor rate, was thus possible over 3 free spectral ranges of the etalon, *i.e.*, about 0.11 nm, before resynchronisation was necessary. Thus, continuous scans over a range up to 0.11 nm with a fundamental bandwidth of 0.001 nm (0.05 nm at <0.001 nm bandwidth when frequency doubled) were possible.

Results and discussion

The performance of the scanning laser system was assessed by experiments on laser-induced fluorescence of prototype molecules—I_2, SO_2 and the transient OH radical. Particular attention was given to wavelength measurements and their reproducibility, evidence for which was obtained from a study of the rotational structure of certain vibrational bands of I_2 near 580 nm. The scanning capability of the laser system in the ultraviolet region was assessed by studies of the $A^2\Sigma^+-X^2\Pi$ transition of OH and of the complex singlet transitions of SO_2 between 310 and 260 nm.

The SO_2 molecule

It was envisaged that SO_2 might be a good prototype molecule for assessing the resolving power and sensitivity of laser fluorescence for concentration measurements using the ultraviolet laser output, and for testing the interface to the flowtube. A tunable dye laser has been used previously to excite fluorescence from the first excited singlet state of SO_2 (260.0 to 325.0 nm) [6]. In this previous study the laser, which had a bandwidth of ~3 cm^{-1}, was used to excite small groups of rovibronic states, and the time dependence of the emission was studied. The kinetic behaviour of these states was surprisingly complex. Brus and McDonald [6] reported the existence of a major, long-lived group of rovibronic states of SO_2 ($\tau > 100 \mu s$) and a minor, short-lived group ($\tau \sim 50 \mu s$). These large variations in radiative lifetime are associated with similar variations in the (low) quantum yield of fluorescence in the near ultraviolet. We examined laser-induced fluorescence from SO_2 in the flow system over various wavelength ranges from 260 nm to 310 nm, and found emission of fluorescence at all excitation wavelengths studied. The sensitivity, in terms of fluorescence intensity as a function of SO_2 concentration, was surprisingly uniform and low throughout the wavelength regions studied. Most of the studies were carried out with a 0.01 nm excitation bandwidth (~1 cm^{-1}), but no large variations in fluorescence intensity could be seen between groups of rovibronic spectral features as might be expected from the results of Brus and McDonald [6]. Generally, the quantum yield of fluorescence throughout the excitation wavelength range was low. We

conclude that further extensive studies of the excited states of SO_2 will be required, and that SO_2 is not a simple prototype molecule for investigation of laser fluorescence. The excitation spectra of SO_2 (at 0.01 nm bandwidth) near 290 nm showed partial rotational structure, which, however, was not fully resolved even using the narrow bandwidth laser excitation (<0.001 nm).

The I_2 molecule

Laser fluorescence of I_2 was observed from a static cell; the pressure of iodine in the cell (typically 10 N m^{-2}) was controlled by varying its temperature. Fluorescence was readily observed both with broadband and narrow band excitation, and it was detected using an S20 photomultiplier cell (EMI 9558QB), provided with a filter (Wratten No. 32) which blocked the wavelength region 520 to 600 nm. Figure 5 shows the composite spectrum of I_2 obtained from five scans of the narrow bandwidth (0.0015 nm) laser excitation wavelength, in which the total fluorescence intensity was monitored as a function of the excitation wavelength. The wavelength range scanned, 581.53 to 581.83 nm, is a complex region of the I_2 $B^3\Pi(O_u^+)-X^1\Sigma_g^+$ spectrum where five strong or medium intensity bands are overlapped. Two additional bands are weak, the 18,2 and 20,3, and these have not been indicated in Figure 5.

Coarse wavelength calibration was carried out using a He−Ne laser to align the dye laser cavity. More accurate wavelengths for the I_2 lines were obtained by calibrating the dye laser wavelength drum using the fundamentals of the known wavelengths of the frequency-doubled OH ultraviolet rotational lines as measured by Dieke and Crosswhite [7]. Some systematic error was inevitable because the calibration was carried out near 564.0 nm (the fundamental corresponding to the OH u.v. lines) rather than at 581.5 nm.

The relative wavelength scale was determined by calibration of the etalon rotation counter, R. In other words, the positions of the counter for successive intensity maxima (spaced by one etalon free spectral range equal to approximately 0.0378 nm at 581 nm) were located. The correct quadratic interpolation of λ as a function of R was calculated, and the resulting interpolation formula was used to determine λ. Because an interferometric wavelength marker was available every 0.0378 nm, even this rather crude interpolation procedure was expected to give relative wavelength measurements to within 0.001 nm (see below).

The spectroscopic constants, as determined by Wei and Tellinghuisen [8], were used to compute the wavelengths of the rotational lines of the B−X system of I_2 (see Table 1). The difference between observed and calculated wavelengths was small, having a mean value of −0.001 nm, which suggests that only small systematic errors were made in the wavelength calibration. Relative wavelength measurements were in agreement within 0.0010 nm, as expected. This agreement between observed and calculated wavelengths also confirms the accuracy of Wei and Tellinghuisen's [8] critical assessment of the spectroscopic data for I_2.
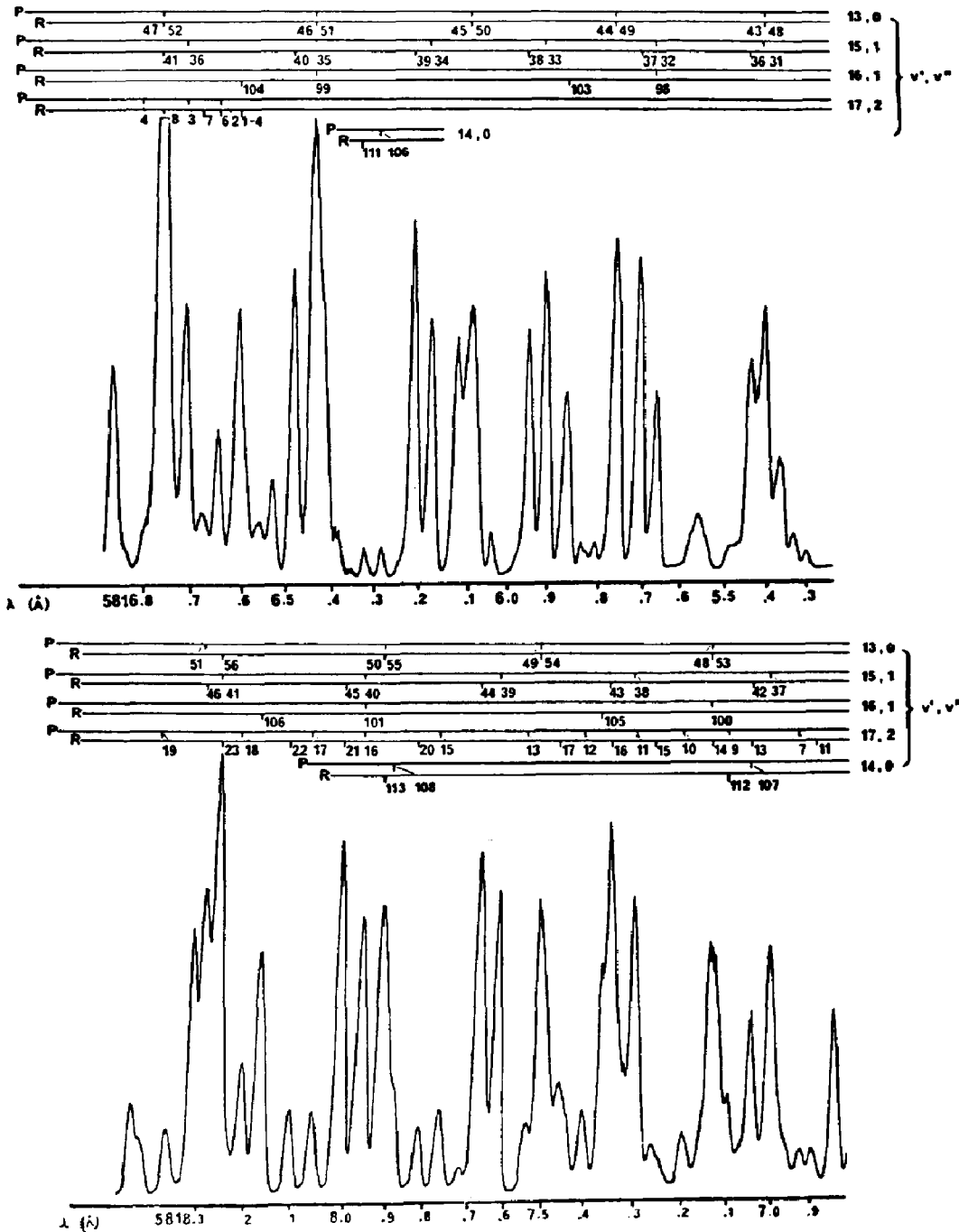
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Fig. 5. Excitation spectrum of I_2 in the wavelength range 581.53 - 581.83 nm using a laser bandwidth of 0.001 nm.

It should be noted that the wavelengths for the I_2 lines calculated using the earlier (and now superseded) spectroscopic constants reported by Steinfeld *et al.* [9] were often 0.05 nm or more different from the

TABLE 1

Wavelengths (nm) of observed rotational lines of I_2 $B^3\Pi(O_u^+)$–$X^1\Sigma_g^+$ using laser-induced fluorescence[*]

J	P(J)			R(J)		
	$\lambda_{observed}$	$\lambda_{calculated}$	$\delta\lambda$	$\lambda_{observed}$	$\lambda_{calculated}$	$\delta\lambda$
31	581.5405	581.5407	—0.0002			
32	.5654	.5660	—0.0006			
33	.5906	.5920	—0.0014			
34	.6168	.6187	—0.0019			
35	.6426	.6462	—0.0036			
36	.6706	.6744	—0.0038	581.5435	581.5443	—0.0008
37	.7004	.7033	—0.0029	.5693	.5697	—0.0004
38	.7303	.7330	—0.0027	.5947	.5958	- 0.0011
39	.7638	.7634	+ 0.0004	.6207	.6226	—0.0019
40	.7939	.7946	—0.0007	.6477	.6502	—0.0025
41	581.8248	581.8265	—0.0017	.6754	.6785	—0.0031
42				.7049	.7075	—0.0026
43				.7354	.7373	—0.0019
44				.7677	.7679	—0.0002
45				.7985	.7991	—0.0006
46				581.8271	581.8311	—0.0040

Typical data (for the 15,1 band) are shown. $\lambda_{calculated}$ is from the work of Wei and Tellinghuisen [8] using our own computations.

observed wavelengths. Also, the PR doublet separations predicted by the constants of Steinfeld *et al.* bore no relation to those experimentally observed in this work.

The OH radical

Hydroxyl radicals, OH $X^2\Pi$, $v'' = 0$, were produced in the flow system by the rapid reaction of hydrogen atoms with nitrogen dioxide,

$$H + NO_2 \rightarrow OH + NO; k_{298} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
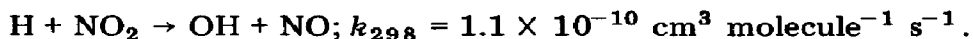
The typical concentration of OH at the fluorescence cell was 2×10^{13} cm^{-3} at a flow tube pressure of 130 N m^{-2}. The fluorescence detector for these studies of OH was a bialkali photomultiplier cell (EMI 6256 SA), provided with an OX1 filter (Chance Pilkington) which transmits in the region 290 to 400 nm. Figure 6 shows the spectrum of the entire 1,0 band (except the S_{21} satellite branch) of OH, $A^2\Sigma^+$–$X^2\Pi$, which was obtained when the exciting line was scanned without the etalon installed, *i.e.* with a laser bandwidth of $\sim$0.008 nm. This spectrum shows all the expected branches and the expected rotational temperature of 300 K. The relative intensities are consistent with the calculated Boltzmann populations of ground state J'' rotational states at 300 K, and with the appropriate line strengths of the (1,0) and (1,1) bands [7]. It was expected that under the conditions of the present work, where the carrier gas is helium and the
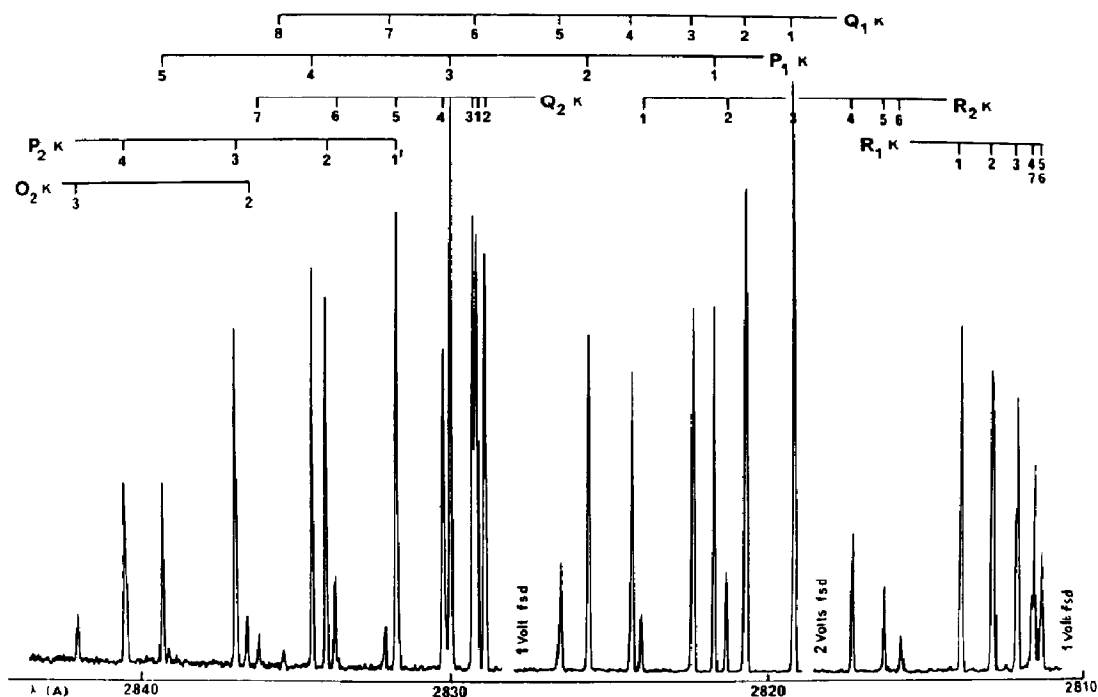
Fig. 6. Excitation spectrum of OH using a laser bandwidth of 0.008 nm. The (1,0) band of the $A^2\Sigma^+$–$X^2\Pi$ transition is shown.

total pressure ~ 130 N m^{-2}, fluorescence occurs predominantly in the 1,1 band (312 - 316 nm) and not in the 0,0 band (306 - 312 nm).

Under these conditions vibrational relaxation of OH $A^2\Sigma^+$, $v' = 1$, by He, within the lifetime of the $A^2\Sigma^+$ state, would be insignificant. This expectation receives confirmation from the work of Lengel and Crosley [10] on the rate of the collisional relaxation of the $v' = 1$ state of OH $A^2\Sigma^+$. On the other hand, at much higher gas densities of predominantly molecular gases, it has been reported [11] that the initial vibrational population (to $v' = 1$) is completely modified by rapid vibrational relaxation, so that predominant emission of laser-induced fluorescence occurs from $v' = 0$.

After installing the etalon to narrow the bandwidth, high resolution spectra near the R_1 band head, Figure 7(a), and the Q_2 band head, Figure 7(b) were obtained. These spectra show clearly the resolved band heads and the satellite lines, and the observed linewidths are limited by the Doppler linewidths of OH, which at 300 K is ~ 0.0008 nm, and not by the laser bandwidth (~ 0.0005 nm).

The resolution of the OH spectrum shown in Figure 7 is superior to that reported by Dieke and Crosswhite in their full study of the A–X system of OH [7]. In particular, the complete resolution in our work of the Q_2 (1) and Q_2 (2) main branch lines from their satellite lines is noted. Probably the main source of inferior resolution in the previous work [7]
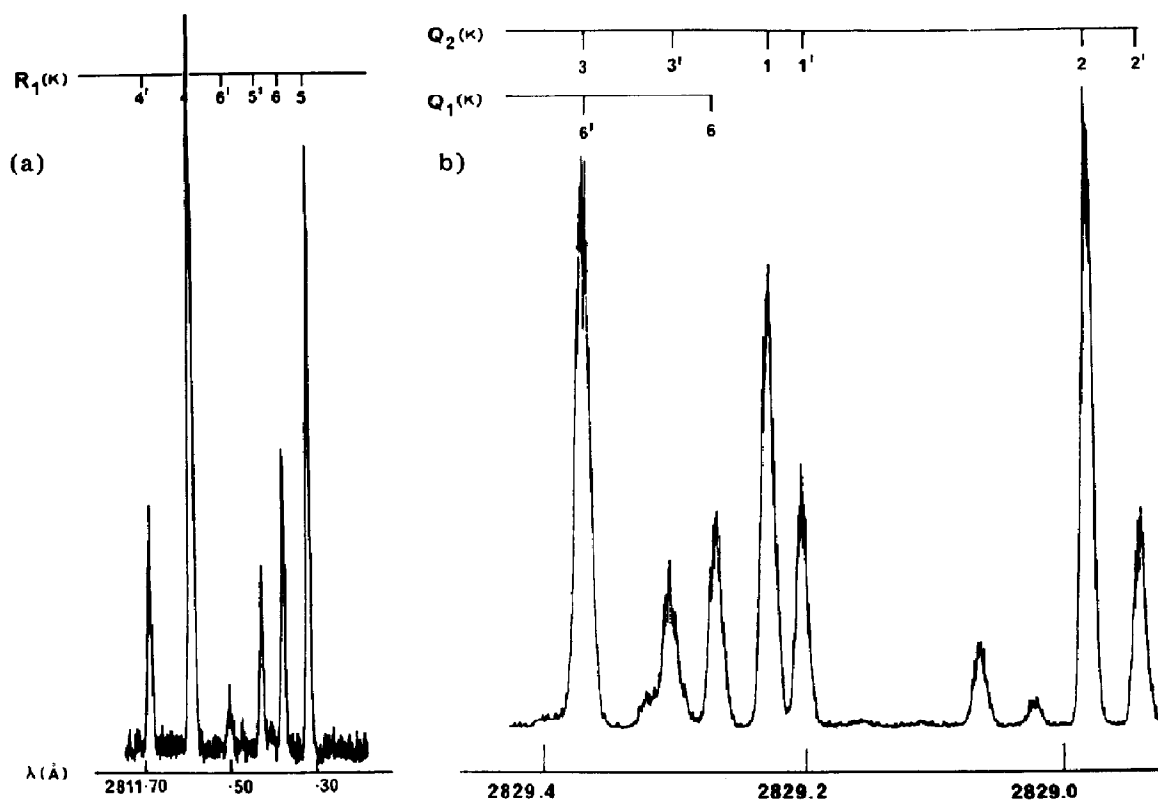
Fig. 7. Excitation spectrum of OH using a laser bandwidth of <0.001 nm. (a) The R_1 band head and, (b) the Q_2 band head in the (1,0) band of the $A^2\Sigma^+$–$X^2\Pi$ transition.

was use of a flame source of OH that had a Doppler width approximately three times greater than that used in the present work. The sensitivity of laser fluorescence as a detector of low concentrations of OH radicals has been pointed out. Various claims for the lower limit of detection of OH concentration have been made, and a conservative estimate for this lower limit would appear to be 10^6 molecules cm^{-3}. In the present work, a considerably higher concentration of OH ($\sim 10^9$ cm^{-3}) was required, but there appears to be no reason why a concentration of 10^6 cm^{-3} should not be detected with our system when more attention is given to baffling and the reduction of scattered light.

The ClO radical

There is considerable current interest in the ClO radical because of its importance in the chemistry of the stratosphere. The most sensitive technique used so far to detect ClO radicals is mass spectrometry, by which concentrations of ClO down to $\sim 10^9$ cm^{-3} can be measured [12]. ClO concentrations can also be determined by optical absorption spectrophotometry at much lower sensitivity [13]. It is clear that any technique with greater sensitivity than mass spectrometry, for the detection of ClO radicals, would have a particular application in monitoring the stratospheric

concentration of ClO, as well as in measuring the rates of reactions of ClO in laboratory experiments. We have therefore attempted to observe laser induced fluorescence of ClO.

The rotational and vibrational structure of the absorption spectrum of ClO, $A^2\Pi_i - X^2\Pi_i$, has been recorded following the flash photolysis of Cl_2 + O_2 mixtures by Durie and Ramsey [14, 16]. The spectrum consists of a progression of red degraded bands which converge near 263 nm. At the long wavelength end of the spectrum the rotational lines of most of the bands are very diffuse owing to predissociation. The band in which the rotational structure is most prominent is the (12,0) with its head at 277.2 nm, although the structure of this band is noticeably diffuse. Also, near the convergence limit the lines appear sharper but they are more closely spaced owing to overlapping of successive vibrational bands. The feasibility of observing fluorescence from ClO will depend primarily on the predissociation lifetime of the upper state.

A concentration of ClO radicals, 10^{13} to 10^{14} cm^{-3}, was produced in the flow system by the reaction,

$$Cl + O_3 \rightarrow ClO + O_2,$$
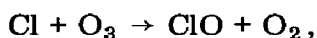
and the ClO was monitored mass spectrometrically. The laser excitation wavelength was scanned from the dissociation limit of the ClO A–X system at 263 nm, to 280 nm. Cut-off filters were used as previously to block the laser wavelength. Even at the maximum sensitivity of our detection system, and with a concentration of ClO $\sim 10^{14}$ cm^{-3}, no fluorescence was observed. The most likely reason for this negative result is that predissociation of the excited state is too strong and the quantum yield of fluorescence is extremely low. Since the rotational lines are noticeably diffuse even in the sharpest part of the ClO spectrum near the convergence limit [14, 16], the predissociation lifetime is likely to be no longer than 300 ps and it is probably around 100 ps in this region. To be consistent with the observed failure to see fluorescence from ClO, the quantum yield of such fluorescence must be $< 10^{-4}$, by comparison with the OH fluorescence. In the absence of quenching, this evidence indicates a radiative lifetime for ClO $A^2\Pi$ ($v' \sim 20$) of > 1 μs. Diffuse vibrational bands of ClO have been observed in emission from flames [15] where the excited $A^2\Pi$ state is no doubt in equilibrium with dissociation products. However, it may still be possible to observe laser fluorescence of ClO with more sensitive detection or in a system where quenching is not important. From a practical standpoint, it is clear that even if weak fluorescence from ClO can be observed, it will not provide a sensitive method of monitoring [ClO].

Conclusions

A continuously scanning narrow bandwidth pulsed laser capable of operation in the visible and the ultraviolet spectrum between 700 nm and 258 nm is described. This instrument has potential for carrying out high resolution spectroscopic studies on molecules at low concentrations. This is likely to be particularly valuable for studies of transient species, such as free radicals, whose maximum available concentrations are severely limited by kinetic constraints.

The facility for continuous scanning has been used, with laser bandwidths of ~ 0.001 nm and ~ 0.015 nm, to record medium and high resolution spectra with high signal to noise ratios in both the visible and the ultraviolet spectrum. It is planned to use a scanning confocal Fabry-Perot interferometer for accurate wavelength measurements (better than 0.0001 nm) of these spectra.

Acknowledgements

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