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ABSTRACT

Strong optically pumped laser action has been obtained in perchloryl fluoride, $FClO_3$, excited by a CO_2 laser. Thirty four new lines were observed between 16.3 and 17.7 microns, with outputs of up to 4 mJ.

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1. Introduction

Molecular lasers operating on vibrational transitions near 16 microns and pumped by a CO_2 laser are of considerable interest for laser isotope separation and laser induced photochemistry. Two such lasers have previously been reported: CF_4 and NOCl (1). We report here strong laser action in perchloryl fluoride, $FClO_3$: this system provides some 34 new lines in the 16.3 to 17.7 micron region with outputs of up to 4 mJ.

2. Experimental

The perchloryl fluoride used in these experiments was obtained commercially and used without further purification. The only impurity noted in low resolution infrared spectra was water vapour, which is frozen out under the laser operating conditions. No difficulties were experienced in handling perchloryl fluoride in conventional vacuum apparatus. However, care must be exercised, as the compound is reported to be highly toxic (2) and is a strong oxidising agent forming explosive mixtures with organic materials (3). Perchloryl fluoride pressures were measured with a capacitance manometer.

The optical layout is shown in figure 1. A modified Lumonix 203 laser was used as the pump. For laser lines above R(32), 60 or 70% reflectivity output couplers were used to optimise the CO_2 laser output of these lower gain lines. Two cooled 2.5 m length temperature-controlled cryogenic gas cells were placed optically in series, with return mirrors as shown. An 8% sample of the laser output is passed via multiple polyethylene and multi-layer filters to a 1 m monochromator, calibrated pyroelectric energy meter or HgCdTe detector as appropriate. All the lines observed were superfluorescent, and the provision of small amounts of optical feedback (an aligned KBr flat prior to the first gas cell) had little effect on the observed outputs. The laser output wavelengths could be measured to ± 0.2 cm^{-1} for strong lines and ± 1 cm^{-1} for very weak lines. The frequencies quoted are corrected to vacuum.

3. Laser Characteristics

Optically pumped laser action is obtained very easily in perchloryl fluoride. At 160 K and 1 Torr pump thresholds were $\lesssim$ 200 mJ for all except the weakest pump lines, R(22) and R(28). Table 1 lists the outputs observed together with the maximum gas cell temperature at which laser action was obtained. A number of lines could only be observed in the 5 m configuration. Close to the cut-off temperatures listed in Table 1 the outputs were weak and sporadic, and maximum output energies were obtained with the gas at a minimum temperature determined by the saturated vapour pressure. The pressure dependence of the total output energy for two typical lines is shown in Figure 2. For strong lines such as R(20) optimum energy is obtained at ~ 3 Torr, and laser action is maintained up to ~ 10 Torr. Weaker lines (e.g. R(28)) have lower optimum pressures typically 1.5 Torr, and cut off at ~ 3 Torr. For specific weak components within a group of lines the optimum pressures are still lower, ~ 0.5 Torr.

Total output energies referred to the cell output were 4 mJ maximum. The laser output energy jitters strongly from pulse to pulse, presumably reflecting changes in the CO_2 laser axial mode structure. In addition to the outputs listed in Table 1 many other weak, sporadic lines were observed. These were particularly numerous for R(34) pumping.

The time dependence of the laser output for most lines is broadly similar to that of the CO_2 laser pump pulse, consisting of an initial 150 ns spike and a 1-2 μs tail. For these lines the time delay between the pump pulse entering the cell and the output pulse was 50-100 ns, compared to a round trip time of 45 ns for the 5 m cells. The gain for these lines is estimated to be ~ 3% per cm. In a few cases (e.g. the R(32) pumped 564.8 cm^{-1} output) there is no spike and the output occurs sporadically, and delayed by up to 2 μs.

4. Discussion

The vibration spectrum of perchloryl fluoride has been studies by several authors (4-8). The modes relevant to laser action (Figure 3) are ν_5 (E) at 589 cm^{-1} and ν_6 (E) at 405 cm^{-1}. The molecule is a symmetric top of point group C_{3v} with $A = 0.2032\ cm^{-1}$ and $B = 0.1755\ cm^{-1}$. Since A and B differ only slightly (owing to the similar masses of ^{16}O and ^{19}F) the molecule approximates to a spherical top, and the parallel and perpendicular bands are of similar appearance, the Q sub branches of the perpendicular bands lying very close to the band origin.

The combination band $\nu_5 + \nu_6$ (Figure 4) has overall species $A_1 + A_2 + E$ of which the A_2 component is not infrared active. The A_1 component frequency may be decreased slightly by weak Fermi resonance with the strong 1063 cm^{-1} fundamental ν_1. Anharmonic constants for this molecule have not been reported, but the form of the vibrations (ν_5, ClO_3 degenerate deformation and ν_6, ClO_3 rock) suggests that negative anharmonic constants are likely. The combination band therefore consists of overlaping parallel and perpendicular components, and the two components are expected to have slightly differing origins, the E component probably lying above the A_1. The band profile is further complicated by the overlapping wing of the ν_1 fundamental and the $\nu_4 - \nu_6$ difference band.

The laser transition is ascribed to $\nu_5 + \nu_6$ $(A_1 + E) \rightarrow \nu_6$ (E) and a very complex structure is to be expected. The $A_1 \rightarrow E$ component is perpendicular, whilst the $E \rightarrow E$ component is a hybrid band. The parallel component of this hybrid band is strongly split owing to the differing Coriolis constants of the upper and lower laser levels(9) and l-type resonance perturbations(11) and Coriolis perturbations(9, 11) are also to be expected. Further complexity arises from the contributions of the two chlorine isotopes ^{35}Cl (76%) and ^{37}Cl (24%). Whilst it is probable that the majority ^{35}Cl species is responsible for most of the observed outputs, the combination of low temperature and low pressure operation with short build up times minimises collisional effects, and the ^{37}Cl species may lase independently. The chlorine isotope shifts for ν_5 and ν_6 are small and not resolvable in low resolution spectra. Reabsorption of lines by the other isotopic species to that pumped almost certainly reduces the output energies and number of lines observed. The use of isotopically enriched ^{35}Cl or ^{37}Cl should therefore improve the laser performance.

In Figure 5 the laser output frequencies are plotted as a function of the CO_2 laser pump frequency. In this plot points lying on a common straight line have the same overall change in rotational state and the intersection point of two or more such lines gives the pump and laser band origins(10). One such line is clearly identifiable in Figure 5 and several other possibilities are indicated. The group of scattered points near 596 cm^{-1} are clearly Q branch outputs. The line intersections indicate two possible pump band origins at 994 cm^{-1} and 1004 cm^{-1} with laser band origins at 588 and 596 cm^{-1} respectively. The absence of a group of Q branch lines for the 588 cm^{-1} component is due to coincidence with the strong ν_5 Q branch absorption at this frequency. The two pump band origins agree well with the maxima marked A and B in the absorption spectrum (Figure 4) and are tentatively identified as the A_1 and E components respectively. These assignments are consistent with the relative positions of the two features and with the fact that the 994 cm^{-1} peak is sharper than the 1004 cm^{-1}. The anharmonicities are negative as expected, but appear rather large. Owing to the complex pattern of Figure 5 other interpretations are possible, and extensive high resolution spectroscopic data are required to permit definite assignments.

5. Conclusions

The perchloryl fluoride laser provides a large number of new output wavelengths in the 16 μm region with substantial output energies. Grating tuning or isotopic substitution would provide further outputs. The pump band of $FClO_3$ is matched better by the 001-020 band output of a $^{13}C^{16}O_2$ laser than by the conventional 001-100 band $^{12}C^{16}O_2$ laser used in this work, and should produce numerous further lines. The spectroscopy of the pump and laser transitions is extremely complex, and merits further study.

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<u>Table 1</u>

Pump Line	Strength	ν cm^{-1}	Max Temp K	Pump Line	Strength	ν cm^{-1}	Max Temp K
R(20)	S	572.8	265	R(36)	M	568.8	280
		573.4				594.6	
						601.9*	
R(22)	VW	605.3*	240			605.4*	
		612.6*					
				R(38)	M	581.6*	280
R(26)	M	576.1	265			600.3	
		588.3				606.3*	
		607.9*					
				R(40)	M	583.1	280
R(28)	W	577.3	190			611.7*	
		596.8					
				R(42)	W**	578.8	280
R(30)	VS	603.8*	280			596.3	
		606.3				606.1	
R(32)	S	564.8*	265	R(44)	VW**		260
		579.5					
		596.9					
		597.8					
R(34)	M	580.7*	280				
		590.7					
		595.6*					
		596.5*					
		603.8*					
		612.2*					

Note: pump lines are $^{12}C^{16}O_2$ 001-100

* only observed in the 5 m configuration

** weak CO_2 pump lines

Strength W weak, M Medium, S Strong, V Very.

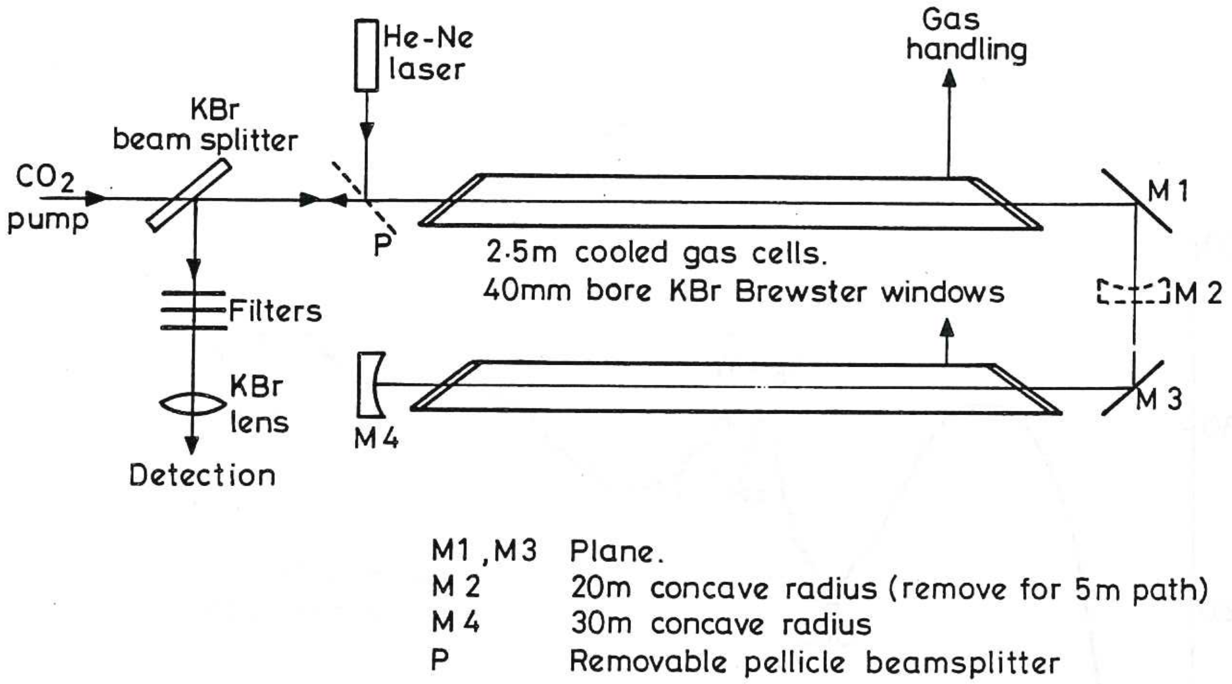

Fig.1 Optical layout.

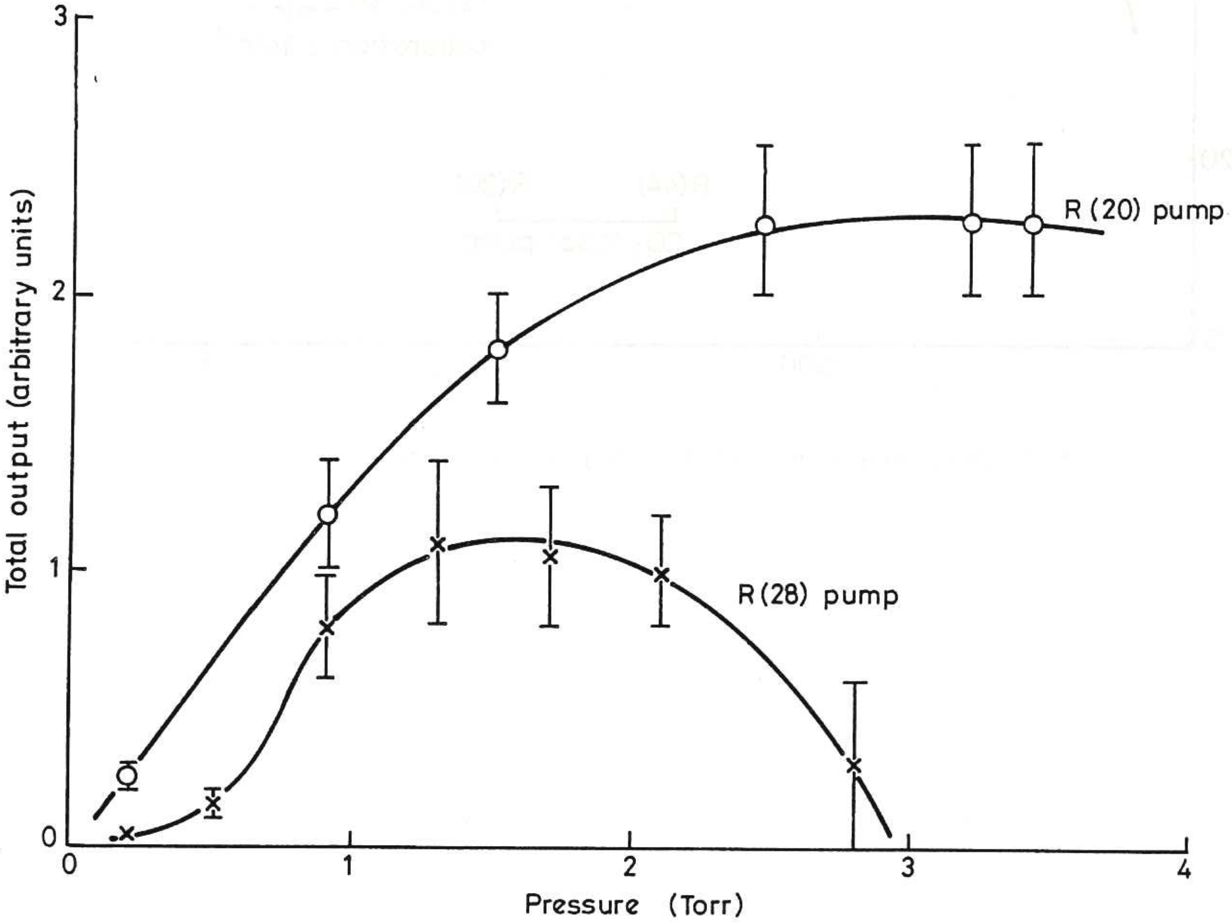

Fig.2 Laser output variation with pressure at 160 K.

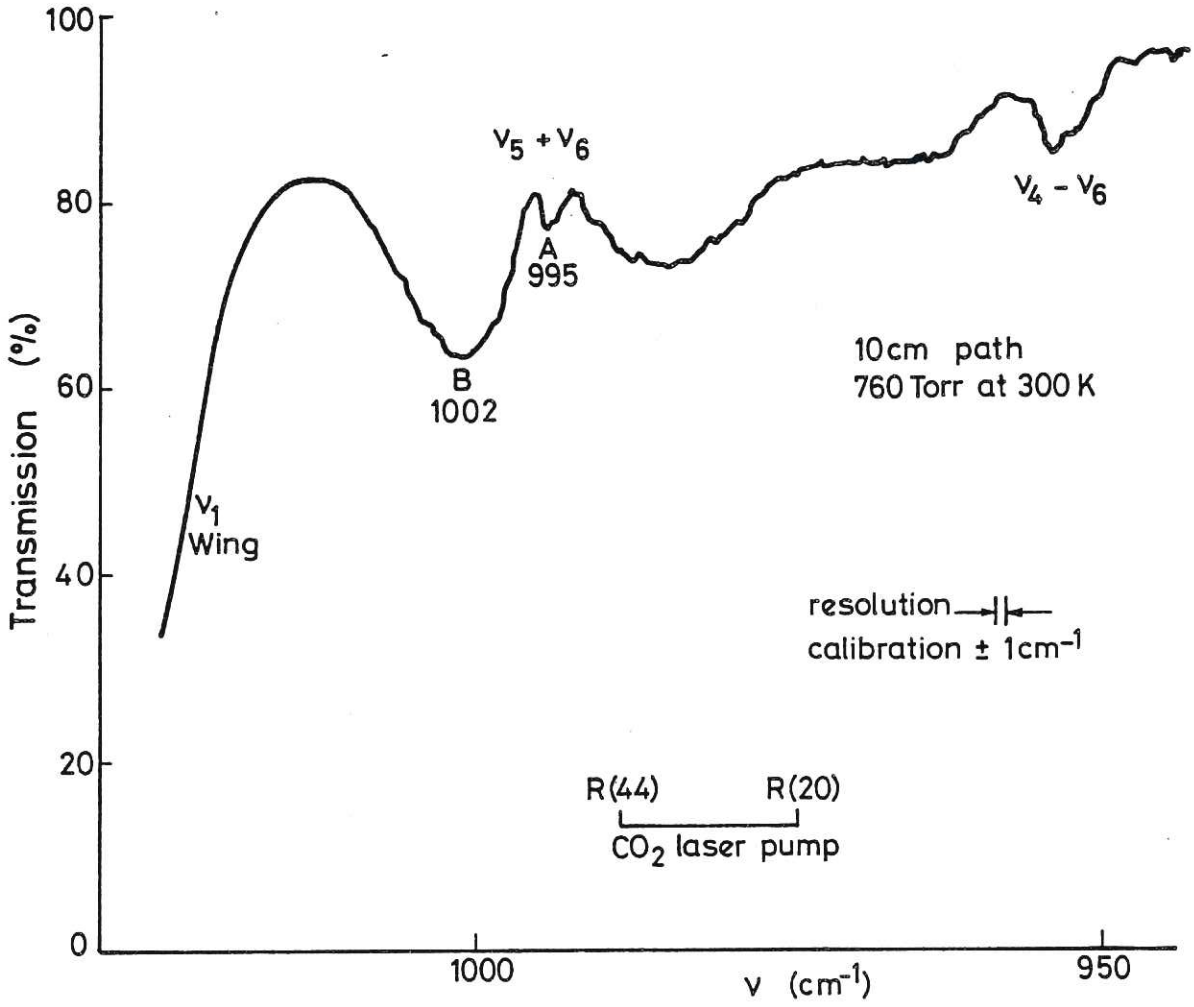

Fig.3 Absorption spectrum of $FClO_3$ in the pump band region.

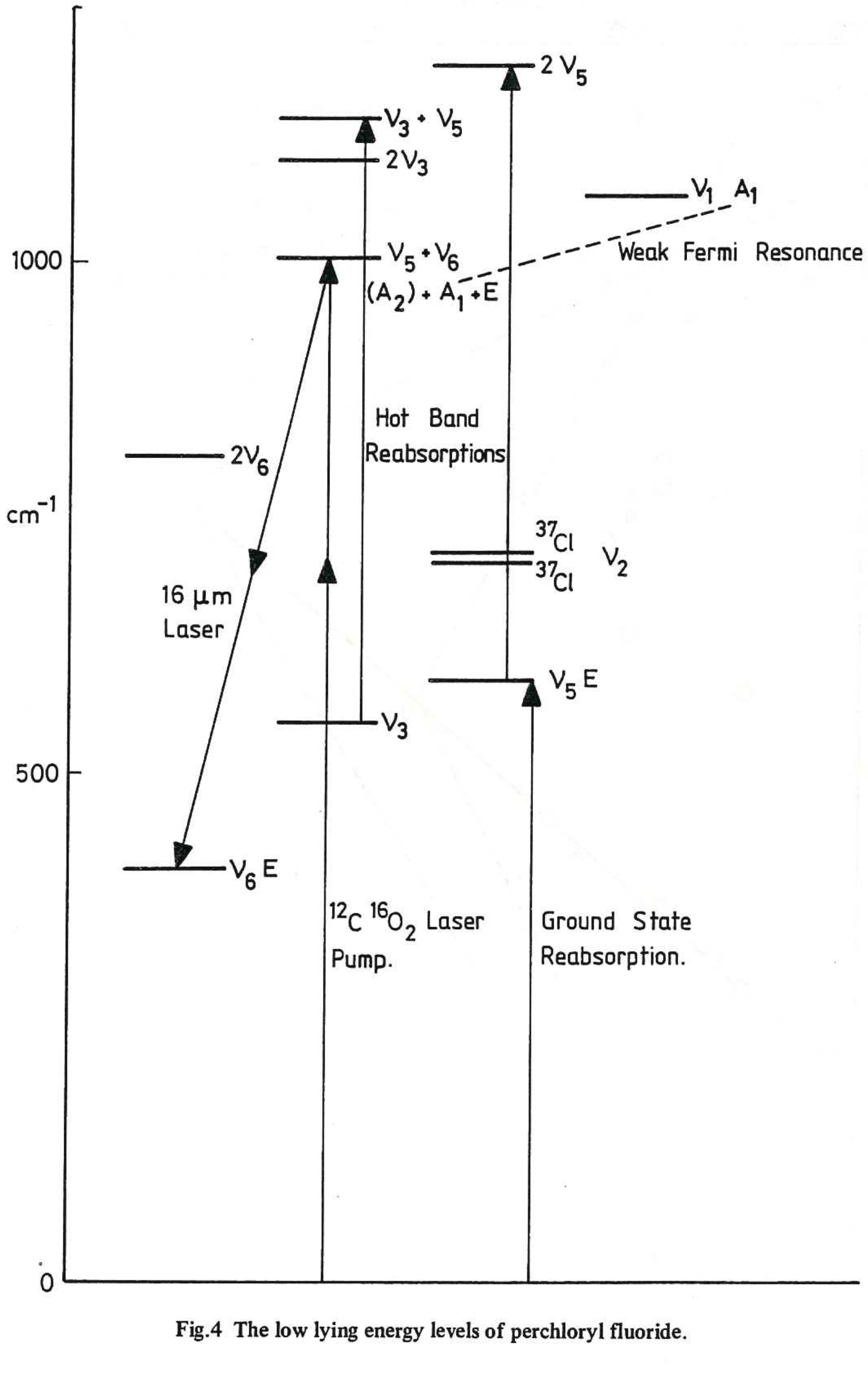

Fig.4 The low lying energy levels of perchloryl fluoride.

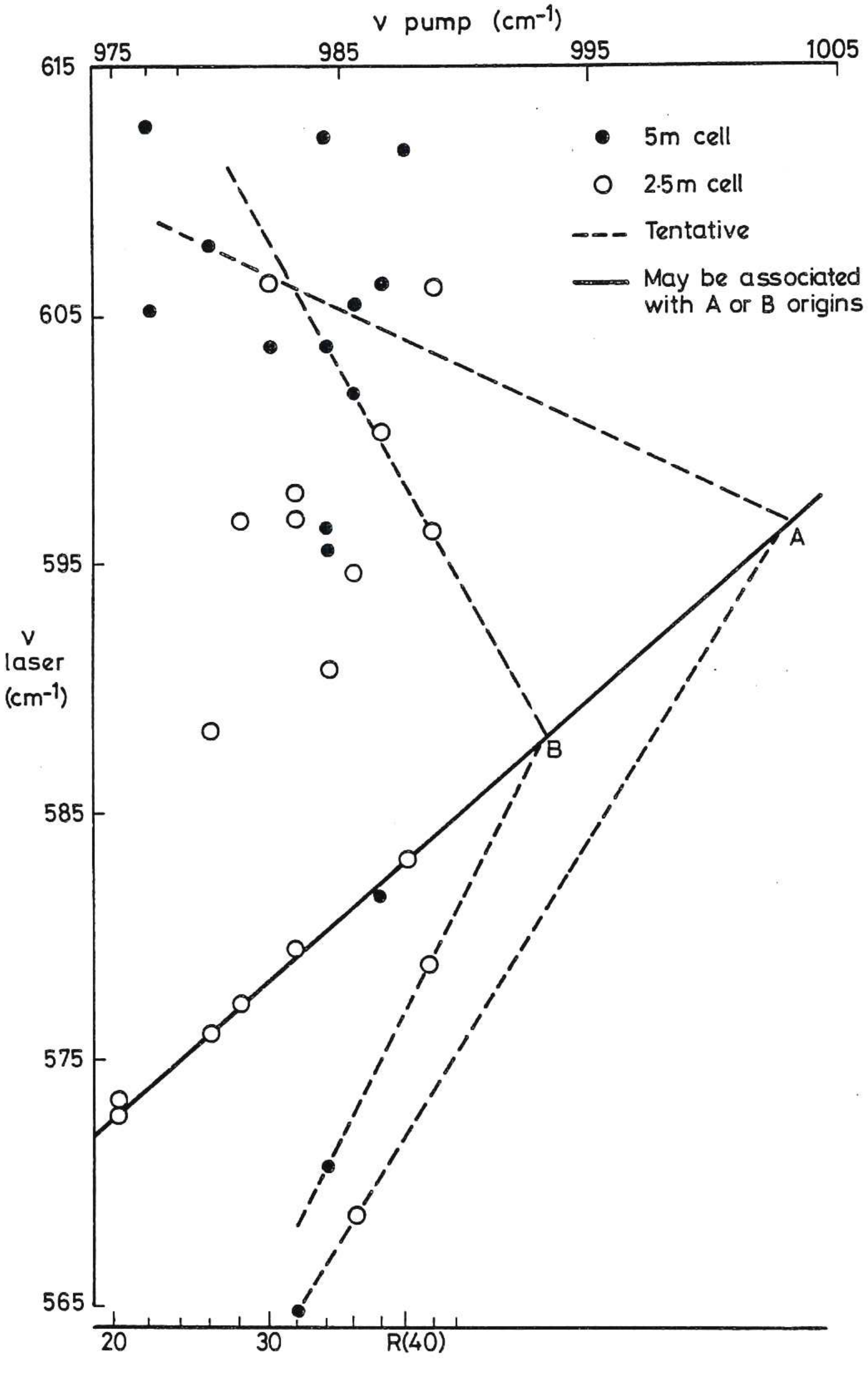

Fig.5 Laser output frequency as a function of pump frequency.