Optically pumped mid-infrared laser action in the monohaloacetylenes

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Abstract

Strong optically pumped laser action excited by a TEA carbon dioxide laser has been obtained from monofluoro-acetylene in the 560-610 cm⁻¹ region with outputs of up to 25 mJ and superfluorescent operation readily achieved without optimisation. These result from excitation of a combination of the two bending modes v4+v5. Laser action was also obtained with 9 μm excitation of the v3 C-F stretch, on a difference band terminating in v4, with similar properties. Lasers of this type are rare. As well as being a potentially useful laser source in a region sparsely populated with good lasers, the results are of interest in the context of ongoing investigations of the spectroscopy of HCCF. Most, but not all lines are assigned. Very weak, erratic laser action was observed from chloro- and bromo-acetylene.

1. Introduction

Optically pumped lasers operating on vibrational transitions are one of the few convenient, powerful sources in the 11-25 μm region. In contrast to the very numerous far infrared lasers operating on pure rotational transitions, for which hundreds of molecular species and thousands of lines are known, relatively few such lasers have been reported. In addition to their intrinsic interest as sources of coherent radiation in this spectral region, laser studies can provide additional spectroscopic information on the molecule concerned. In particular the simultaneous observation of the pump frequency (normally accurately defined by the pump laser wavelength) together with the observed output frequencies frequently provides unambiguous identification of the levels concerned.

The monohaloacetylenes fluoro-, chloro- and bromo-acetylene, have pump bands accessible to the carbon dioxide laser which are suitable for vibrational transition lasing. The spectroscopy of fluoro-acetylene in particular has been very extensively studied in recent years as an example of an asymmetric linear model whose ro-vibrational spectroscopy can, hopefully be completely understood in considerable detail. There has previously been one report of far infrared, pure rotational lasing in HCCF pumped by a cw laser [1], on just two lines, one pumped by ¹²C¹⁸O₂, but vibrational transition lasing has not previously been reported.

¹ The experimental results reported were obtained whilst the author was at AEA Technology, Culham Laboratory, Abingdon, Oxon, OX14 3DB, UK.
2. Experimental

The optically pumped laser system used has been described in [2] in detail. Briefly it comprises one or two temperature-controlled copper gas cells 2.5 m x 40 mm diameter with KBr Brewster angled windows, optically in series, pumped by a line tuneable, modified Lumonics model 203 TEA CO₂ laser. The HCCF laser outputs only obtainable in the double cell configuration are noted in the tables. The pump laser provided up to 5 J multi-axial multi-transverse mode output on the strong CO₂ lines at 1 Hz, and has an estimated bandwidth ~ ±1.5 GHz, ie, ±0.045 cm⁻¹ on strong lines, narrowing on transitions well away from the J = 20 peak. The pump pulse was of a typical ~100 ns gain switched ‘spike’ and ~500 ns ‘tail’ shape. It should be noted that techniques for suppressing unobserved far infrared or mm wave laser action [3] were not in use during these experiments. Outputs were measured with fast MCT detectors, wavelengths determined to better than ±0.5 cm⁻¹ for strong lines, ±1 cm⁻¹ for weak lines, with a 1 m monochromator, and energies determined with a pyroelectric energy meter. For the more accurately determined lines the correction due to the refractive index of air is marginally significant (~0.16 cm⁻¹ at 600 cm⁻¹) and is included in the figures quoted. The halocetyl enes were stable under CO₂ laser irradiation for many hours. No particular difficulties were experienced in handling and using the gases despite their pyrophoric nature (see Appendix.) Gas fills could be used over many days with no noticeable degradation.

Pressures were measured with a capacitance manometer and gave no evidence of gas decomposition. Laser action was obtained in superfluorescent mode very easily from HCCF.

2.1. 10 μm pumped lines of fluoro-acetylene

The observed CO₂ pump lines and laser outputs are listed in Table 1. The relative strengths shown in this table are the comparative strengths within a group emitted when pumped with a given carbon dioxide laser line. As noted in Table 2, whilst the strongest outputs were obtained with the gas cells cooled to 163 K, laser output was readily observed with the cells at 315 K, slightly above room temperature, and in-deed some lines are only observed with the gas cell warm. Here the relative strength compares the outputs emitted in response to different carbon dioxide laser pump lines. The pressure dependence of two typical lines is shown in Fig. 1. The stronger lines typically give maximum outputs at 400–650 Pa, whilst weaker lines benefit from lower pressures ~100 Pa. For the 10 R(24) pumped lines at room temperature and optimum pressure the output energy was ~25 mJ. The system was not optimised for energy output in terms of pump power density, feedback etc. and it is likely that considerable higher efficiencies could be obtained. Most lines showed an output pulse similar in shape to the TEA laser pulse with very little delay; in a few cases (e.g. 10R18 pumped 607.6 cm⁻¹ output) only the ‘spike’ output occurs with no ‘tail’.

2.2. 9 μm pumped lines of fluoro-acetylene

Superfluorescent laser action pumped by 9 μm region CO₂ laser lines was unexpectedly observed from HCCF, with the gas at 173 K and 90 Pa. The observed lines are listed in Table 3 and their temperature dependence in Table 4. The outputs lie in the region of second order grating responses to the pump wavelength; these were carefully eliminated with appropriate filters. With the exception of the 9P(12) and 9R(12) pumped outputs the output wavenumbers were coin-
Table 1

<table>
<thead>
<tr>
<th>$^{12}$C$^{16}$O$_2$ Pump line</th>
<th>$^{12}$C$^{18}$O$_2$ Pump frequency cm$^{-1}$</th>
<th>HCCF pump feature cm$^{-1}$</th>
<th>HCCF pump transition</th>
<th>Laser output frequency cm$^{-1}$</th>
<th>Calculated laser frequency cm$^{-1}$</th>
<th>Laser transition</th>
<th>Relative strength in group</th>
</tr>
</thead>
<tbody>
<tr>
<td>10R(24)</td>
<td>978.4722</td>
<td>978.487</td>
<td>R(36) (a)</td>
<td>586.6</td>
<td>586.496</td>
<td>Q(37) f*(i)</td>
<td>M</td>
</tr>
<tr>
<td>10R(20)</td>
<td>975.9304</td>
<td>975.978</td>
<td>R(23) f(c)d?</td>
<td>?</td>
<td>559.325</td>
<td>P(37)f*(i)</td>
<td>S</td>
</tr>
<tr>
<td>10R(18)</td>
<td>974.6219</td>
<td>974.605</td>
<td>R(35)f(b)</td>
<td>560.3</td>
<td>604.9</td>
<td>R(21)c*</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>974.609/</td>
<td>R(21)c(e)</td>
<td>594.2</td>
<td>606.711</td>
<td>R(35)f*(i)</td>
<td>M</td>
</tr>
<tr>
<td>10R(16)</td>
<td>973.2885</td>
<td>973.283</td>
<td>R(29) f(a)</td>
<td>606.4</td>
<td>606.449</td>
<td>R(29)f*(i)</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td>973.301</td>
<td>R(25)f(d)</td>
<td>586.4</td>
<td>586.401</td>
<td>Q(30)f*(i)</td>
<td>W</td>
</tr>
<tr>
<td>10R(10)</td>
<td>969.1395</td>
<td>969.132</td>
<td>R(19)c(d)</td>
<td>587.9</td>
<td>587.627</td>
<td>Q(20)c*</td>
<td>W</td>
</tr>
<tr>
<td>10R(6)</td>
<td>966.2504</td>
<td>966.298</td>
<td>R(15)f(d)</td>
<td>587.6</td>
<td>587.760</td>
<td>Q(16)f*</td>
<td>W</td>
</tr>
<tr>
<td>10P(14)</td>
<td>949.7930</td>
<td>949.456</td>
<td>R(23)f(e)</td>
<td>583.2</td>
<td>583.124</td>
<td>P(5) f*(i)</td>
<td>VS</td>
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<td></td>
<td>966.166</td>
<td>P(5) f(a)</td>
<td>588.9</td>
<td>588.962</td>
<td>R(3)f*</td>
<td>W</td>
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<tr>
<td>10P(28)</td>
<td>936.8037</td>
<td>936.819</td>
<td>P(21)f(e)</td>
<td>570.2</td>
<td>570.228</td>
<td>P(21)f*</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td>936.798</td>
<td>P(21)f(b)</td>
<td>596.8</td>
<td>596.818</td>
<td>R(19)f*</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td></td>
<td>936.803</td>
<td>P(31)c(d)</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*: e, f not reliably resolvable; closest transition given, or e-e, f-f assumed. ?: Upper state laser coincidence with f; laser transitions fit e better, at the error bar limits. (a) v4+v5, $\Sigma^+$; (b) v4+v5, $\Delta$; (c) 2v4+v5, $\Pi$; (d) 2v4+v5, $\Pi$; (ii) v4+v5, $\Delta$; (iii) 2v4+v5, $\Pi$; (iv) v4+2v5, $\Pi$; (v) v4+2v5, $\Pi$.

Table 2

Temperature dependence of the 10 $\mu$m pumped lines

<table>
<thead>
<tr>
<th>$^{12}$C$^{16}$O$_2$ Pump line</th>
<th>Observed at 163 K</th>
<th>Behaviour at 163 K</th>
<th>Observed at 303 K</th>
<th>Behaviour at 303 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10R(32)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10R(24)</td>
<td>✓</td>
<td>VS</td>
<td>✓</td>
<td>VS</td>
</tr>
<tr>
<td>10R(22)</td>
<td>✓</td>
<td>VS</td>
<td>✓</td>
<td>VS</td>
</tr>
<tr>
<td>10R(20)</td>
<td>✓</td>
<td>W Erratic</td>
<td>✓</td>
<td>W Erratic</td>
</tr>
<tr>
<td>10R(18)</td>
<td>✓</td>
<td>S</td>
<td>✓</td>
<td>S</td>
</tr>
<tr>
<td>10R(16)</td>
<td>✓</td>
<td>VS</td>
<td>✓</td>
<td>VS</td>
</tr>
<tr>
<td>10R(12)*</td>
<td>✓</td>
<td>W Erratic</td>
<td>✓</td>
<td>W Erratic</td>
</tr>
<tr>
<td>10R(10)*</td>
<td>✓</td>
<td>W Erratic</td>
<td>✓</td>
<td>W Erratic</td>
</tr>
<tr>
<td>10R(8)*</td>
<td>✓</td>
<td>M</td>
<td>✓</td>
<td>M</td>
</tr>
<tr>
<td>10P(8)*</td>
<td>✓</td>
<td>VVW Erratic</td>
<td>✓</td>
<td>VVW Erratic</td>
</tr>
<tr>
<td>10P(14)</td>
<td>✓</td>
<td>W</td>
<td>✓</td>
<td>W</td>
</tr>
<tr>
<td>10P(28)</td>
<td>✓</td>
<td>S</td>
<td>✓</td>
<td>W</td>
</tr>
</tbody>
</table>

*: Only observed with 5 m path.

searches failed to locate it. A number of cross checks were made on the 565 and 585 cm$^{-1}$ outputs to ensure their validity (eliminating ghosts of second order pump laser lines, etc.) confirming their wavenumbers as given. The 477.7 cm$^{-1}$ outputs were 'spike' only, the other outputs showed sporadic, fluctuating 'tails' with a stronger 'spike'.

2.3. Chloro- and bromo-acetylene

Chloro- and bromo-acetylene proved to be extremely weak and erratic optically pumped lasers. For chloro-acetylene, optically pumped laser action was observed pumped by 10P(36), 10P(34) and 10P(28). The outputs were confirmed to lie in the 600-700 cm$^{-1}$ region with filters, and the 10P(36) emission was observed at ~ 603 cm$^{-1}$, although this may be one component of a multi-line output.

In all cases the outputs were extremely sporadic, occurring on a few per cent of pump pulses and with low (microjoule region) outputs. For chloro-acetylene operating conditions were typically ~ 180 K and 90 Pa. Attempts were made to enhance the output of the 10P(36) pumped line of HCCCI by providing feed-
Table 3
9 µm pumped lines in HCCF

<table>
<thead>
<tr>
<th>12C¹⁸O₂ pump line</th>
<th>13C¹⁸O₂ pump frequency cm⁻¹</th>
<th>13C¹⁸O₂ pump feature cm⁻¹</th>
<th>HCCF pump transition</th>
<th>Laser output frequency cm⁻¹</th>
<th>Calculated frequency cm⁻¹</th>
<th>Laser transition</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>9R(20)</td>
<td>1078.5906</td>
<td>1078.560</td>
<td>R(27) (a)</td>
<td>477.7</td>
<td>476.65</td>
<td>Q(28) (i)</td>
<td>S</td>
</tr>
<tr>
<td>9R(12)</td>
<td>1073.2784</td>
<td>1073.274</td>
<td>R(18) (a)</td>
<td>477.8</td>
<td>477.40</td>
<td>Q(19) (i)</td>
<td>VVS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>565.7</td>
<td>584.6</td>
<td>477.7</td>
<td>VV</td>
<td></td>
</tr>
<tr>
<td>9R(10)</td>
<td>1071.8837</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S, Erratic</td>
<td></td>
</tr>
<tr>
<td>9P(6)</td>
<td>1058.9487</td>
<td>1058.840</td>
<td>*Q(10) e, f (c)</td>
<td>?</td>
<td>NOT 477.7</td>
<td>VW, 300 K</td>
<td></td>
</tr>
<tr>
<td>9P(12)</td>
<td>1053.9235</td>
<td>1053.999</td>
<td>P(16) (b)</td>
<td>?</td>
<td>584.8</td>
<td>Total S</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>565.3</td>
<td>584.8</td>
<td></td>
<td>W</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Other, ?</td>
<td></td>
</tr>
<tr>
<td>9P(14)</td>
<td>1052.1955</td>
<td>1052.155</td>
<td>P(14) (a)</td>
<td>477.7</td>
<td>477.75</td>
<td>Q(13) (i)</td>
<td>S</td>
</tr>
<tr>
<td>9P(16)</td>
<td>1050.4412</td>
<td>1050.454</td>
<td>P(13) (c)</td>
<td>?</td>
<td></td>
<td>VW, Erratic</td>
<td></td>
</tr>
<tr>
<td>9P(18)</td>
<td>1048.6608</td>
<td>1048.721</td>
<td>P(19) (a)</td>
<td>477.7</td>
<td>477.47</td>
<td>Q(18) (i)</td>
<td>S</td>
</tr>
</tbody>
</table>

(a) v3, Σ⁺ → Ground state; (b) v3 + v5, Π ← v5, Π; (c) v3 + v4, Π ← v4, Π; (i) v3, Σ⁺ → v4, Π; * and other nearby low JQ lines.

Table 4
Temperature dependence of the 9 µm pumped lines

<table>
<thead>
<tr>
<th>12C¹⁸O₂ pump line</th>
<th>Observed at 163 K</th>
<th>Behaviour</th>
<th>Observed at 303 K</th>
<th>Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>9R(20)</td>
<td>√</td>
<td>VVS</td>
<td>√</td>
<td>S</td>
</tr>
<tr>
<td>9R(12)</td>
<td>√</td>
<td>S Erratic</td>
<td>√</td>
<td>S Erratic</td>
</tr>
<tr>
<td>9R(10)</td>
<td>√</td>
<td>VV</td>
<td>√</td>
<td>W Erratic</td>
</tr>
<tr>
<td>9P(14)</td>
<td>√</td>
<td>VS</td>
<td>√</td>
<td>VV</td>
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<td>9P(16)</td>
<td>√</td>
<td>VW Erratic</td>
<td>√</td>
<td>VS</td>
</tr>
<tr>
<td>9P(18)</td>
<td>√</td>
<td>VS</td>
<td>√</td>
<td>S</td>
</tr>
</tbody>
</table>

Fig. 2. Low lying energy levels of HCCF.

back from aligned KBr of Ge flats; the KBr flat (weak feedback) gave very sporadic, stronger outputs whilst the germanium flat (strong feedback) gave more consistent, weaker outputs. Manipulating the CO₂ laser spectrum with an intra-cavity low pressure CO₂ hot gas cell to force off CO₂ line centre pumping [4], or with an intra-cavity low pressure gain cell to give narrow band line centre pumping failed to improve the performance. This remained the case with increased reflectivity (70%) output couplers on the CO₂ pump laser which improved the pump energy to 2 J for these high-J lines.

Bromo-acetylene proved even more difficult to use than chloro-acetylene. With pressures of 100 Pa and the operating temperature set to give saturation at this pressure some very occasional weak outputs were observed when pumping with high P-branch lines of the 10 µm CO₂ laser band.

In view of the extremely poor performance of these two laser systems work on them was not continued.

3. Discussion

3.1. Spectroscopic background

The infrared and microwave spectroscopy of the monohaloacetylenes has been studied for many years.
Ref. [5] obtained complete fundamental vibrational assignments for the three compounds in 1961. Later studies [6] provide details of overtone and combination bands relevant to laser action in HCCBr and HCCI. More recently extensive high resolution studies have been made [7-9] of the infrared spectra of fluoro-acetylene, and microwave data providing precision rotational constants are available [10-12]. The low lying modes of HCCF are shown in Fig. 2.

Limited data from laser spectroscopy [12,16,17] and from far infrared laser transitions [1] is also available. In this far infrared work only two lines were observed. One pumped by $^{12}$Cl$^{18}$O$_2$ 9R(12) was assigned but the only far infrared $^{12}$Cl$^{16}$O$_2$ pump line, 9R(18), did not give rise to mid-infrared laser action and was only assigned with some uncertainty to the doubly hot band v5 + v3 + 2v5. These limited far infrared data are thus not of direct help in assigning the mid-infrared lines.

More recently the spectroscopy of HCCF has received quite intensive study, particularly with respect to molecular 'quasi linearity' [18], the 'vibron' model [19], detailed Hamiltonians of quasilinear molecules [20] very high lying states [22,23] and equilibrium structures [24-26].

In predicting pump and laser transitions the constants and model from [20] are probably most accurate, but do not cover all the required states or lend themselves to easy calculation. Since the pump laser bandwidth ($\sim 0.045$ cm$^{-1}$) and limited accuracy of laser frequency measurement ($\sim 0.5$-1 cm$^{-1}$) limit the utility of extreme accuracy in calculating transition frequencies we have used the constants from Refs. [21,22] which are the most comprehensive available and use the conventional rotational model.

Since our laser data on HCCBr and HCCI is very limited we do not review here the infrared spectroscopy of these materials in detail. In general data for these molecules is much less complete than for HCCF.

CO$_2$ laser line frequencies are taken from Ref. [27].

3.2. 10 $\mu$m pumped lines of fluoro-acetylene

These were the original target of the work on the halocetylenes, pumping of the combination band v4 + v5 (the two doubly degenerate bending modes) closely parallels the very successful C$_2$D$_2$ laser [28].

The outputs pumped by 10R(24, 29) and P(14) are easily assigned to the expected II component of the combination state, with v5 as the lower level. The R branch pumped lines excite rather high J pump transitions, and rotational redistribution favours relatively high operating temperatures. In contrast the P(14) pumped line excites P(5) and both rotational redistribution and reduction in lower laser level population favour low temperature operation and the transition is not seen at room temperature.

The output pumped by 10R(18) is complex. Two pump transitions lie very close by, R(35) of v4 + v5, $\Delta$ and the hot band R(21) of 2v4 + v5, II + v4, II. The outputs confirm that both states are involved, although a difficulty arises with the delta state assignment. The output wavenumbers are in better agreement with the $\Delta^e$ upper state, although the pump transition is clearly assigned as f from the existing constants. The e,f splitting is at the limit of our error bar for frequency determination, but the discrepancy appears to be real, and is consistent for both the P and R branch lines. In the constants used [22,23] for this $\Delta$ state the B$_e$, B$_f$ splitting is only one digit in the last significant figure ($10^{-7}$ cm$^{-1}$), i.e. the conventional I type doubling is negligibly small, and the split arises from a substantial difference in the distortional D parameter at this very high J = 35. This may be a case in which a more complex Hamiltonian is needed to satisfactorily model the pump band. A further output at 594.2 cm$^{-1}$ pumped by this laser line is unassigned. The transition to the delta state is formally forbidden by the delta I selection rule, but at high J (35) such transitions become allowed through interactions, and similar effects are seen in C$_2$D$_2$.

The other pump transitions aside from 10R(20) pumping are all readily assignable on the basis of the combined pump and laser frequencies to hot band pumped states, favouring room temperature operation in general. Where several nearby pump transitions exist (some examples are given in Table 1) the output frequencies serve to distinguish between them. For 10R(6) pumping there appear to be additional, unassigned features in the absorption spectrum in the vicinity, but the satisfactory agreement of pump and output frequencies supports the assignment.

For 10R(20) excitation the output was not determined as it was weak and erratic. The possible assignment given in Table 1 is at the extreme limit of
frequency offset we have observed in any system. It is more likely that this transition belongs to some as yet unanalysed, weak pump band.

3.3. 9 μm pumped lines of fluoro-acetylene

The 9 μm region of the fluoro-acetylene spectrum is dominated by the fundamental absorption to v3 and various weak hot bands based on v4, v5, 2v4, 2v5, v4+v5 etc. The form of the modes is that v3 is the C–F stretch, v4 the C–H bending mode, and v5 the C–F bend. Pumping a fundamental transition is a good candidate for far infrared laser action, but mid-infrared outputs require a difference band laser transition if v3 is excited. Very few such optically pumped lasers are known, the low gain on such difference transitions generally precluding laser build up within the inversion lifetime (∼ 100 ns at ∼ 150 Pa, set by rotational relaxation).

The majority of the outputs occur, to within experimental error, at 477.7 cm⁻¹, and coincide exactly with the calculated position of the v3→v4 difference band Q branch; the Q branch width is too narrow to resolve. This feature has never before to our knowledge been observed in absorption spectroscopy of HCCF; since the lower state (v4) population at 300 K is nearly 7% this is surprising, despite its rather low frequency. The corresponding sum band, v3+v4, has been observed, but is weak with ∼ 25% absorption at the Q branch peak with 2260 Pa in a 7.85 m path. [22] Published spectra of HCCF do not cover the difference band region, but the lack of any reference to it in the extensive spectroscopic studies of the molecule would suggest the band is at best weak. Low resolution spectra (∼ 4 cm⁻¹) taken at 300 K in our laboratory with a 10 cm path length at 10000 Pa show a very weak ‘PQR’ structure centred on ∼ 480 cm⁻¹ with a peak absorption on the Q branch ∼ 2%, just visible in the shoulder of the KBr window roll-off. High resolution spectra (∼ 0.2 cm⁻¹) taken at 65 Pa in a 2 m path show a Q branch only peaking just below 478 cm⁻¹, 15% absorption and a barely resolved width of ∼ 0.4 cm⁻¹. P, R branches are not reliably observable under these conditions owing to low signal to noise ratios. Ref. [8] notes that the hot band v3+v5 (the combination with the C–F bending mode) is anomalously strong compared to the v3 fundamental, and speculated as to the mechanisms and their relevance to difference band strengths, but there have been no further studies of these effects, and the mode involved in laser action is v4, the C–H bend. These very weak bands suggest that an Raman type mechanism is involved, and the ‘spike only’ output pulse shape supports this, although the pump laser to HCCF frequency offsets are small enough to suggest actual inversion. Further work is needed to clarify the mechanisms involved in these transitions.

The 9P(12) pumped outputs are unassigned and present considerable difficulties. The output was strong and consistent in total energy, but was not at or near 477.7 cm⁻¹. Weak outputs were located at ∼ 565 and 584 cm⁻¹, which appear consistent with a v4 transition. There is almost certainly a further output line which we did not locate which carries most of the energy; location of outputs at very unexpected frequencies can be very difficult and time consuming with a low repetition rate pump laser, 1 Hz in our case. One possible mechanism which could lead to emission on v4 after pumping on v3 would be excitation of the v4→v3+v4 hot band followed by laser action on v3+v4→v3, although we are not aware of any example of such a system. The bands of this type in HCCF based on v4 and v5 are well characterised, and there is no credible pump transition involving v4. Similar remarks apply to the subsidiary weak outputs pumped by 9R(12).

Although we did not locate the very weak and erratic 9P(6) pumped outputs there is little doubt that the pump transition is Q(10) of v3+v4 ←→ v4, II as the computed coincidence is excellent. The Q branch of a II to II transition only has significant strength for low J lines, in agreement with the calculated coincidence.

3.4. Chloro- and bromo- acetylene

No detailed analysis of these weak lasers is possible. The general location of the pump lines in the high P branch of the carbon dioxide laser 10 μm band, and of the outputs in the 600–700 cm⁻¹ region with one line in the vicinity of 603 cm⁻¹ from chloro-acetylene, identify the pump band as v4+v5 and the laser transition as v5. The ∼ 603 cm⁻¹ HCCl line is almost certainly the Q branch of v4+v5←→v5. For these molecules pumping of v3, the carbon-halogen stretch, by a carbon dioxide laser is not possible as they lie at too low a frequency. The low frequency of
the lower laser level, causing substantial thermal pop-
ulation at the lowest temperatures possible by bulk
cooling these relatively involatile species, combined
with the effect of mixed isotopic composition for chlo-
rine and bromine, are responsible for their poor per-
formance.

4. Conclusions

Fluoro-acetylene forms a useful and simple opti-
cally pumped laser source in a region sparsely pro-
vided with convenient lasers. Although the material
must be handled with care, in practice we found it
straightforward and trouble free to make, store and
use the gas. Without any significant optimisation
output energies of 25 mJ were easily achieved. Us-
ing off line centre tuned pump lasers, and control
of mid-infrared/far infrared laser interactions more
transitions and higher energies could undoubtedly be
achieved.

The majority of the output transitions can be as-
signed. However despite the very extensive spectro-
scopic studies of the material a number of transitions
cannot be identified. These may involve some of the
few low lying states for which spectroscopic constants
are not available. A surprising result is the very strong
emission on the v3→v4 difference band, which has
not previously been observed in absorption spectra as a
hot band; optically pumped lasers of this type are rare.

It is possible that unobserved laser action occurring
in the far infrared and mm wave region may be occur-
ing, and involved in the transitions without obvious
assignments. We have considered several such inter-
actions which fail to provide explanations. For the 9
µm pumped bands the combination of a strong pump
band with high pump laser intensity will lead to sub-
stantial 'power broadening', which may be involved in
the unexpected v3→v4 laser transition mechanism.

The 10 µm pumped emissions are in the 560–610
cm⁻¹ region, corresponding to a change in the v4 ex-
citation. Since the upper states involve v4+v5 and v5
is also infrared allowed, lasing on a v5 transition cen-
tred on 380 cm⁻¹ would probably be possible with
appropriate windows (CsI, KRS5) and an absorber to
suppress the v4 transition; the multi-phonon absorp-
tion bands of high resistivity silicon, a readily available
optical material transparent at ~ 380 cm⁻¹, would be
suitable.

Although our results for chloro- and bromo-
acetylene are limited and show poor performance it
is possible that further optimisation – in particular off
line centre tuning of the pump laser and the use of
isotopic pump laser lines – could render these systems
useful.

Appendix. Synthesis of the haloacetylenes

Initial attempts to synthesize the haloacetylenes
proved troublesome. Ref. [29] describes modific-
tions to earlier methods for bromoacetylene and
chloroacetylene. Unfortunately, following Bashford
et al.'s route we obtained negligible yields of chloro-
acetylene, whilst for bromo-acetylene the yield was
significant but heavily mixed with many other hydro-
carbons and brominated hydrocarbons which proved
difficult to separate.

Fluoro-acetylene was easily synthesized by a mod-
ification of the process described by Middleton et al.
[30]. Fluoro-maleic anhydride (prepared as a custom
synthesis by Lancaster Synthesis Ltd) was allowed to
fall dropwise into a 300 mm long vertical silica tube
packed with short pieces of silica small bore tubing,
externally heated to 933 K. The resulting gas passed
through a trap held at ~ 190 K and was then con-
densed in a liquid nitrogen cooled trap. On comple-
tion of the addition of fluoro-maleic anhydride the fur-
nace was cooled and the liquid nitrogen cooled trap
raised to ~ 190 K. The resulting gas flowed through a
300 × 20 mm diameter column of soda-asbestos, and
was collected in a liquid nitrogen cooled bulb. The en-
tire apparatus was connected to a trapped rotary pump
during these operations.

Yields were substantial although not quantitative as
described by Middleton. Since various authors have
described liquid and gaseous haloacetylenes as liable
to spontaneous decomposition and even as 'treacher-
ously explosive' [30] suitable precautions were ob-
served, although no explosions occurred. The only im-
purities detectable by infrared spectroscopy were trace
levels of 1,1 difluoro-ethylene and acetylene.

Success with fluoro-acetylene led us to attempt the
same method starting from chloro- and bromo-maleic
anhydride. Despite the lower stability of these com-
pounds the method was again successful, although with somewhat lower yield. No attempt was made to optimise the furnace temperature, and the optimum may be lower for these materials. The heavier halo maleic anhydrides are readily commercially available, sometimes mixed with maleic anhydride. This is unimportant as the low boiling point pyrolysis products of the maleic anhydride are CO, CO₂ and C₃ H₃. The first two are removed by the existing process, and the third by suitable trap to trap distillation. For the bromo- and chloro-compounds only trace levels of acetylene were detectable as an impurity.

This process provides a reliable, trouble-free source of the halo acetylenes. We found the materials stable over long periods if stored in darkened pyrex vessels with PTFE taps. Bromo-acetylene is certainly violently pyrophoric, and all three materials are best prepared in small quantities and treated as hazardous, especially when condensed for recovery or distillation, etc.

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