INFRARED STUDY OF TRANSIENT MOLECULES IN CHEMICAL LASERS

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The Ninth European Congress on Molecular Spectroscopy is devoted mainly to infrared and Raman spectroscopy. However, the present paper will be concerned with a rather novel kind of infrared spectroscopy, the study of the emissions from chemical lasers. This work was initiated in the course of rapid scan infrared spectroscopy with more conventional aims of molecular spectroscopy. It is an appropriate subject for this Congress because molecular spectroscopists will surely be able to contribute richly to this field and because the consideration of possible new frontiers of spectroscopy is in the tradition of this excellent Congress.

INTRODUCTION

In a chemical laser, the population inversion results directly from the distribution of reaction heat among the available degrees of freedom in the course of an elementary reaction process. Hence, in principle, chemical laser pumping might excite electronic, vibration–rotation or pure rotational laser transitions. Electronic population inversions can be expected to be rather rare since most electronic transitions involve rather high energies relative to reaction heats. Rotational population inversions may be produced in many reactions but even if they are, they will be difficult to maintain because of the rapidity of rotation–translation equilibration. Vibrational excitation escapes both of these difficulties. Only moderate energies are needed and vibrational equilibration can require many thousands of molecular collisions. Hence there are rich possibilities for chemical lasers involving vibrational population inversions.

It is gratifying that such population inversions hold quite interesting information about elementary chemical processes. The initial placement of reaction heat in vibrational degrees of freedom has important consequences in the chemistry of the reaction products. In the most dramatic example, an explosion, the activation of vibrational degrees of freedom can effectively withhold a significant fraction of the reaction heat, moderating the temperature rise during the crucial induction period.

A brief indication of experimental techniques will be presented, followed by a review of the systems that have been successfully studied.

EXPERIMENTAL TECHNIQUES

In principle, a chemical laser is most simply activated in a flow system. In fact, such laser action has been sought since 1961 by Polanyi and coworkers[1] when their infrared fluorescence studies of the hydrogen atom–chlorine reaction indicated that vibrational population inversions were obtainable. Flow systems have been relatively unyielding, however, compared to the flash-initiated chemical reactions with which the first chemical lasers were discovered by Kasper and Pimentel[2, 3]. Hence, only the flash techniques will be described, though flow systems hold great interest and they deserve and will receive much attention in the next few years.

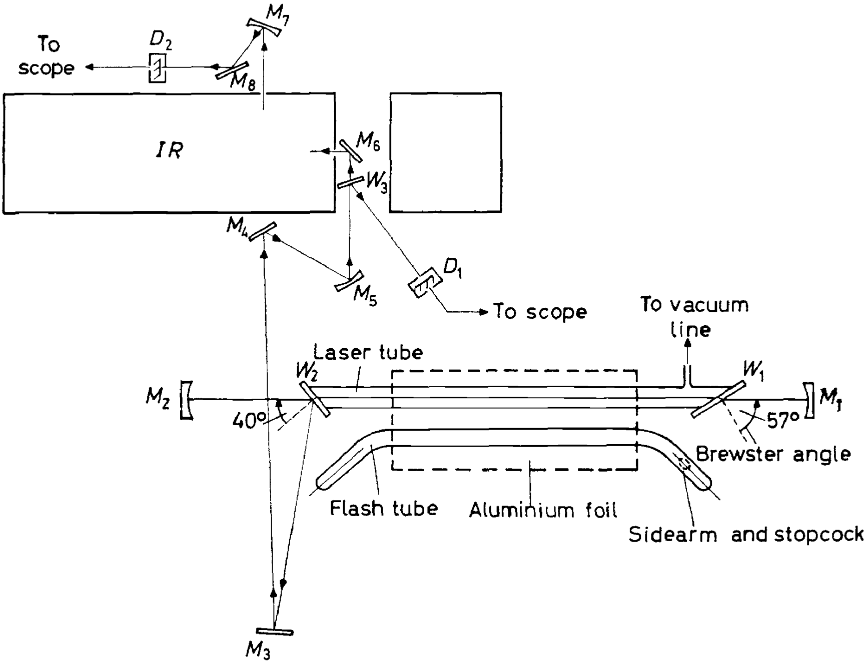

Figure 1. Schematic representation of flash-initiated chemical laser equipment[4]: M_1, M_2—spherical gold-coated laser cavity mirrors; M_3, M_4, M_6, M_8—plane, aluminium-coated mirrors; M_5, M_7—spherical, aluminium-coated mirrors; W_1, W_2—polished NaCl windows, 4 mm thickness; W_3—sapphire window, 2 mm thickness; D_1, D_2—photoelectromagnetic InSb detectors; *IR*—commercial IR monochromator

Figure 1 is a simple schematic representation of the apparatus used by Corneil and Pimentel in their continued study of the hydrogen–chlorine explosion laser[4]. As shown in sequential assembly in *Figure 2*, a quartz laser tube fitted with Brewster-angle windows is placed in a laser cavity alongside a conventional photolysis flash lamp. An optical cavity using spherical mirrors is convenient because alignment is relatively uncritical compared to that of planar mirror laser cavities. A small helium–neon laser is a considerable aid in this alignment. Gold mirrors can be used over a wide infrared spectral range and a fraction of the laser emission can be deflected out of the cavity either by a reflection plate or a laser tube window set slightly off the Brewster angle.

The flash photolysis unit poses no requirements not already highly developed for conventional flash photolysis studies. Flash energies in the range of a few hundred to a few thousand joules are needed as well as flash durations of a few tens of microseconds. Flash durations as long as a few

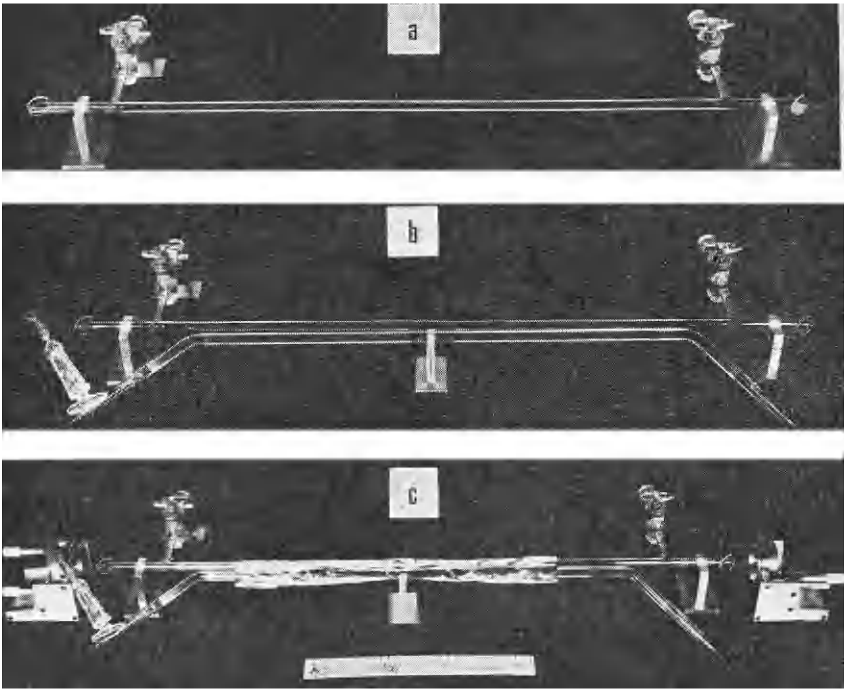

Figure 2. Sequential assembly of flash-initiated chemical laser: a. Quartz laser tube fitted with polished NaCl windows set at Brewster angle: b. Flash tube placed alongside laser tube: c. Micrometer-controlled laser mirror mounts added to define laser optical cavity; aluminium foil around laser and flash tubes for optical coupling; centimetre scale for reference

tenths of a millisecond are ineffective, evidently because of unfavourable competition with quenching processes, including vibrational deactivation.

The pulsed laser emission obtained in flash-initiated systems requires a rapid response detector, though not particularly high sensitivity. We have used an indium-antimonide photoelectromagnetic detector (Honeywell, DLG64B2) at room temperature for most of our work, though occasionally the higher sensitivity of a cooled (20° or 4°K) mercury- or gold-doped germanium detector has been useful. It is valuable to divide the laser emission into two fractions, one of which is recorded on a detector as a measure of total laser emission while the other is passed through a monochromator and recorded on a second detector. The two signals are simultaneously presented on a two-trace oscilloscope and, of course, photographed.

PHOTODISSOCIATION AND PULSED DISCHARGE DISSOCIATION LASERS

When a molecule is electronically excited to a repulsive state, either through absorption of light or a collisional process in an electric discharge, the resulting bond rupture raises the same energy-distribution questions as a conventional chemical reaction. By the definition we have given, this would not constitute a chemical laser because the energy source for population inversion is in the first instance a quantum of light or an energetic collision. Nevertheless, we should not be so semantically preoccupied that we ignore the chemical information to be gained from such lasers. Furthermore, the discovery and development of photodissociation lasers is interlaced with that of chemical lasers.

In 1964, Kasper and Pimentel[2] reported the first such laser, ironically, the only system to be mentioned in the present paper that involves electronic excitation. A search for vibrational excitation of CF_3 fragments from CF_3I photolysis was diverted by the discovery that the iodine atom is born almost exclusively in the $^2P_{1/2}$ excited state.

$$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{1/2}) \tag{1}$$

The $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition gave stimulated emission light pulses up to the kilowatt range with a duration of a few microseconds. The frequency is 7604 cm^{-1}, wavelength 1·315 μ. Similar behaviour was quickly discovered for a variety of alkyl iodides and perfluoroalkyl iodides[5]. The CF_3I system displayed gains in excess of 100 dB/metre and demonstrated the potentialities of chemical processes (simple bond rupture in this case) for high population inversions. In fact, this system was exploited by De Maria and Ultee[6] who were able to develop laser pulses of millisecond duration, of total energy as high as 65 joules and with peak power approaching 100 kilowatts.

Table 1 shows progress since 1964. During 1966, Pollack (Bell Laboratories) added a photodissociation laser based upon photolysis of nitrosyl chloride. Nitric oxide produced from ClNO emits laser transitions in the 6 μ region. Fifteen lines were observed with power up to 10 watts.

In concurrent research, Deutsch (Raytheon) discovered that nitrosyl chloride in a pulsed electrical discharge also produces nitric oxide laser emission in the 6 μ region[8]. He measured 60 lines up to excitation as high

Table 1. Photodissociation and pulsed discharge dissociation lasers

Year	*Parent*	*Excitation*	*Excited species*	*Frequency range* (cm^{-1})	$v' \rightarrow v''$ *transitions observed*	*Author and reference*
1964	CF_3I	flash $h\nu$	$I(^2P_{1/2})$	7604	$^2P_{1/2} \rightarrow {}^2P_{3/2}$	Kasper and Pimentel[2]
1965	C_2F_5I, C_3F_7I, CH_3I, C_2H_5I, C_3H_7I, C_4H_9I	flash $h\nu$	$I(^2P_{1/2})$	7604	$^2P_{1/2} \rightarrow {}^2P_{3/2}$	Kasper, Parker and Pimentel[5]
1966	ClNO	flash $h\nu$	NO†	1593—1679	6 → 5 up to 9 → 8	Pollack[7]
	ClNO	pulsed discharge	NO†	1560—1710	6 → 5 up to 11 → 10	Deutsch[8]
	OCS	pulsed discharge	CO†	1760—1970	7 → 6 up to 14 → 13	Deutsch[9]

as $v = 11 \rightarrow 10$ with frequency accuracy near $\pm 0{\cdot}05$ cm^{-1}. To obtain a satisfactory fit to his own data as well as existing spectroscopic data, he found it necessary to refine the vibrational parameters of nitric oxide and offers the best present estimate, $\omega_e = 1904{\cdot}01$ cm^{-1} and $\omega_e x_e = 13{\cdot}995$ cm^{-1}.

With OCS in the pulsed discharge, Deutsch found laser emission due to vibrationally excited carbon monoxide[9]. He attributes this excitation to the dissociation of electronically excited OCS*

$$OCS^* \longrightarrow CO^\dagger + S \tag{2}$$

It seems plain that secondary chemical reactions that can occur in a pulsed discharge will furnish a variety of additional laser systems. However, chemical information might be difficult to extract from them because of the energy-rich situation, the uncertain temperature, and the multiplicity of processes that occur in a discharge. On the other hand, the possibility of rapid repetition rates (10 to 16 pulses per second have been used[8, 9]) offers some of the advantages of a continuous laser, both in study of its properties and in its use as a light source.

The photodissociation lasers, on the other hand, give a more interpretable chemical process. Information concerning the excited state derived from the other types of spectroscopic studies will often be available and useful. In principle, monochromatic photolysis light could be used and vibrational excitation in the fragmentation process can be elucidated. In fact, an important result may already have been derived. It has long been postulated that vibrational excitation is improbable in a chemical reaction if the energy is 'released' or distributed between the fragments as they separate, i.e., if the fragments divide the energy as they are repelled from each other. However, the ClNO laser produces nitric oxide containing as much as 50 kcal of vibrational excitation (up to $v = 9$). If ClNO is photolytically excited to a repulsive state, as seems most likely[7], then we have a case in which the vibrational excitation occurs during separation in a repulsive state[10].

CHEMICAL LASERS

The elucidation of the CF_3I photodissociation laser provided the key to previously confusing, but intense infrared emissions from hydrogen–chlorine explosions observed by Kasper and Pimentel using rapid-scan infrared techniques. These emissions were then readily identified with laser emission from the secondary chemical reactions that occur in a photolytically-induced H_2–Cl_2 explosion[3].

$$Cl_2 + h\nu \longrightarrow 2Cl \tag{3}$$

$$Cl + H_2 \longrightarrow HCl + H \quad \Delta H = +1 \text{ kcal} \quad \Delta H^{\ddagger} = 4{\cdot}4 \text{ kcal} \tag{4}$$

$$H + Cl_2 \longrightarrow HCl^\dagger + Cl \quad \Delta H = -45 \text{ kcal} \quad \Delta H^{\ddagger} = 2 \text{ kcal} \tag{5}$$

Since reaction (5) is the only possible pumping reaction, this system represents the first operative chemical laser. There seems no doubt, however, that the homogeneous and virtually instantaneous initiation of the explosion is an important element in its operation. For example, an H_2–Cl_2 mixture which gave laser emission at flash energies as low as 700 joules with flash pulses of 15 μsec half-height duration failed to give any emission with a

Table 2. Chemical lasers

Year	*Parent*	*Initiation*	*Excited species*	*Frequency range* (cm^{-1})	$v' \rightarrow v''$ *transitions observed*	*Author and reference*
1965	H_2, Cl_2	flash $h\nu$	HCl†	2604–2698	2 → 1	Kasper and Pimentel[3, 4, 12]
1965	D_2, Cl_2	flash $h\nu$	DCl†	1935–1959	2 → 1	Corneil and Pimentel[4, 12]
	HD, Cl_2		HCl†, DCl†	1947–2652	2 → 1	
	CS_2, O_2	flash $h\nu$	CO†	1761–1961	6 → 5 up to 14 → 13	Pollack[14]
1967	H, Cl_2	flow	HCl†(a)	—	2 → 1, 3 → 2, 4 → 3	Anlauf *et al.*[13]
	H, Br_2	flow	HBr†(a)	—	3 → 2, 4 → 3, 5 → 4	
	Cl, HI	flow	HCl†	—	2 → 1, 3 → 2, 4 → 3	
	UF_6, H_2	flash $h\nu$	HF†	3435–3623	2 → 1	Kompa and Pimentel[15]
	UF_6, D_2		DF†	2594–2725	2 → 1, 3 → 2	
	Cl_2, HI	flash $h\nu$	HCl†	2572–2675	1 → 0, 2 → 1, 3 → 2	Airey[16]
	Cl_2, HI	pulsed discharge	HCl†	2400–2675	2 → 1, 3 → 2	Moore[17]

(a) Spontaneous emission only.

1200 joule flash extended over a 150 μsec half-height duration. This first chemical laser initially seemed to give a result in discord with the vibrational rate constants determined by Airey *et al.*[11] in infrared fluorescence studies. The discrepancy was relieved, however, when, first, Corneil was able to show that the H_2–Cl_2 laser emission consisted entirely of 2 → 1 transitions[12] rather than 1 → 0, as initially proposed[3], and second, when subsequent measurements by Anlauf *et al.*[13] cast doubts on the earlier[11] fluorescence values of both ratios, $k_{v=2}/k_{v=1}$ and $k_{v=1}/k_{v=0}$.

Table 2 lists chronologically the chemical laser systems that have been operated since the first chemical laser. The separate listing of the D_2–Cl_2 and HD–Cl_2 may seem redundant but it makes an important point. A year of experimental effort was required after the report of the H_2–Cl_2 laser before a DCl laser was successfully operated[12]. Despite the apparent similarity of the H_2–Cl_2 and the D_2–Cl_2 explosion lasers, significant factors act to lower the gain of the DCl laser relative to the HCl laser. These factors will generally be influential in new chemical laser systems, so that they warrant consideration. Most obvious is the effect of the increase in the moment of inertia. Since rotational equilibration can be expected, the density of rotational states dilutes the inversion density of any particular rotational transition for a given vibrational transition. By itself, this factor lowers the DCl gain by a factor of about two relative to HCl.

The mass effect has a second deleterious effect in increasing the density of the vibrational states. Relative to HCl, there will be approximately $\sqrt{2}$ times as many vibrational states sharing in the distribution of reaction heat. Furthermore, the vibrational transition probability of DCl is lowered by a factor of 2 relative to HCl, another factor that directly affects the gain.

Finally, but less easily evaluated, is the influence of isotopic mass on reaction rates. All processes that compete with the build-up of population inversions (particularly, collisional deactivation) are favoured by a reduction of the rates of reactions (4) and (5).

These factors, so vividly demonstrated in the HCl and DCl laser contrast, will always be important in evaluating a potential new laser system: density of rotational states, vibrational spacing, transition probability, and reaction rates. The first two factors will probably be the most significant obstacles to the development of polyatomic chemical lasers.

The CS_2–O_2 flash-initiated explosion laser is of special interest, as the second chemical system that displayed laser emission. This system is extremely prolific in laser emissions: thirty-one transitions were observed by Pollack[14] with vibrational changes extending from $v = 6 \rightarrow 5$ to $14 \rightarrow 13$. Rather low peak powers (~20 milliwatts) are appropriate to the high moment of inertia of CO. As will be noted later, these laser transitions are informative concerning the chemistry of the carbon disulphide-oxygen explosion.

The persistent efforts of Polanyi and coworkers have finally culminated in laser emission in a chemical flow system[13]. Practically, of course, the energy input is large because a glow discharge source of hydrogen or chlorine atoms is needed. Nevertheless, we have in the Cl–HI system a prototype 'pure' chemical laser in which laser action results from the mixing of two chemical substances and the subsequent chemical processes.

The UF_6–H_2 chemical laser takes advantage of the low moment of inertia of HF and the effectiveness of UF_6 as a photolytic fluorine atom source[15]. Two reactions could contribute to the population inversions observed ($v = 2 \rightarrow 1$ for HF and both $3 \rightarrow 2$ and $2 \rightarrow 1$ for DF).

$$UF_6 + h\nu \rightarrow F + UF_5$$

$$F + H_2 \rightarrow HF + H \qquad \Delta H = -32\ \text{kcal} \tag{6}$$

$$H + UF_6 \rightarrow HF + UF_5 \qquad \Delta H \simeq -46\ \text{kcal} \tag{7}$$

The high gain (18 dB/metre) and low pressure threshold (0·05 mm UF_6 + 0·09 mm H_2 with a 1600 joule flash) indicate the favourable combination of variables in the HF laser and they forecast the discovery of a variety of HF chemical lasers.

The Cl_2–HI system has given HCl laser emission both through photolysis[16] and pulsed discharge[17] and involves both reactions (5) and (8)

$$Cl + HI \rightarrow HCl + I \qquad \Delta H = -32 \tag{8}$$

Once again, the photolytically initiated laser has the advantage over the pulsed discharge in that photolysis of HI can be eliminated by suitable filtering of the photolysis flash. Then only reaction (8) would contribute to the population inversion, simplifying interpretation.

ENERGY DISTRIBUTION IN ELEMENTARY CHEMICAL REACTION STEPS

Surely one of the most interesting applications of chemical lasers is the deduction of energy partition among the available degrees of freedom in elementary reaction processes. Such information furnishes one of the most promising frontiers of chemical kinetics and there are few alternative avenues toward it. Enormous equipment investments are implied by the molecular beam technique and its applicability is at present rather limited by detector specificity. Infrared fluorescence study is laborious and requires a sophisticated kinetic and spectroscopic attack. Theoretical calculations still are limited to simple systems, despite the advent of complicated computer programmes. Hence, the fact that chemical lasers will themselves be limited to favourable systems does not detract from the importance of this new tool.

We can already list significant information concerning reaction excitation of vibrational degrees of freedom. In the most valuable type of interpretation, all of the kinetic processes that influence the population inversion should be considered. Only for the hydrogen–chlorine system has this been attempted (to our knowledge) and the difficulties are formidable[4]. There remains value, however, in the simplest view possible, the computation of the percentage of reaction heat that can enter a vibrational mode with high probability, as indicated by the highest vibrational quantum number found as a laser upper state. *Table 3* shows the results accumulated already, only two and a half years after the advent of this type of study.

The striking aspect of the tabulated results is, of course, the very high fraction of the reaction heat that *can* enter vibrational modes. These percentages must be evaluated, of course. The *average* percentage **is** likely to be quite a bit lower, but it can be argued that it is probably not as much as a factor of two lower in most cases, still a large fraction of the available energy. If low quantum numbers are involved (2 or 3), there are few states lower with which to share the energy. For example, in the $H + Cl_2$ reaction, the $v = 2$ state is as heavily populated as the $v = 1$ state (as shown in the $2 \rightarrow 1$ laser emission) and the $v = 1$ state requires exactly half the energy of the $v = 2$ state. Whether the average is above or below half depends then upon the relative magnitude of k_2 and k_0. It seems improbable that k_2 is comparable to k_1 but k_0 is much larger than k_2. More reasonable would be a monotonic effect of v on excitation from $v = 2$ to 1 to 0, so that the average would be near half the $v = 2$ percentage shown in *Table 3.* The CS_2–O_2 laser, on the other hand, presents the other extreme, very high vibration quantum numbers. Here the experimental data already indicate that the most intense laser emission involves quantum numbers near 9 or 10, somewhat larger than half the maximum value. Again the average energy can be less than half the $v = 14$ value only if there were an unlikely increase in k_v for v below 5.

Table 3. Maximum observed percentage of reaction heat transferred into vibration

	ΔH	*max. v′*	*% of ΔH in vib'n.*	*Ref.*
$D + Cl_2 \rightarrow DCl^\dagger + Cl$	−45	2	32	12, 4
$H + Cl_2 \rightarrow HCl^\dagger + Cl$	−45	2	45	3, 12, 4
$Cl + HI \rightarrow HCl^\dagger + I$	−32	3	70	16
$F + H_2 \rightarrow HF^\dagger + H$	−32	2	80	15
$SO + CS \rightarrow CO^\dagger + S_2$	−54	(max, 11)(a)	—	14
$O + OCS \rightarrow CO^\dagger + SO$	−59	(max, 12)(a)	—	(a)
$O + CS_2 \rightarrow CO^\dagger + S_2$	−83	14	84	14
$F + D_2 \rightarrow DF^\dagger + D$	−32	3	85	15

(a) Maximum vibrational excitation possible is below the highest vibrational excitation observed, $v' = 14$.

We must offer one more caveat concerning the results in *Table 3.* These percentages show that vibrational excitation receives a large fraction of reaction heat *among those reactions for which laser emission has been observed.* Obviously reactions that do not give significant vibrational excitation will not be represented in *Table 3.* Hence generalization is not warranted. This limitation does not detract a bit, however, from the importance of these experimental results in guiding us as we frame theoretical models for these same systems.

CONCLUSIONS

Much remains to be done in exploiting the chemical lasers already known and in adding to the list. It is clear that the spectroscopist's art and the kineticist's insight will couple well in this field. Much progress can be expected in the next few years and chemical lasers will take a significant place both in laser techniques and in chemical kinetics.

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