

INFLUENCE OF PHOTOCHEMISTRY ON CH₃I PHOTODISSOCIATION LASER PERFORMANCE*

ANGEL COSTELA, JUAN M. FIGUERA, MARGARITA MARTÍN[†] and LUIS VALLE
Instituto de Química Física "Rocasolano", C.S.I.C., Serrano, 119, Madrid-6 (Spain)

(Received April 6, 1979; in revised form August 29, 1979)

Summary

A study of the products formed in the operation of the CH₃I photodissociation laser was carried out. The influence of several factors — the introduction of buffer gases, the wavelength of the flash irradiation and the flash energy — are reported.

Experimental conditions that allow laser "repetitive" operation are discussed. The formation of largely translationally excited CH₃ rather than vibrationally excited CH₃ at $\lambda > 220$ nm and the opposite at $\lambda < 220$ nm is shown and its influence on laser quenching is described. The relevance of the rate of I₂ diffusion in the laser operation is noted.

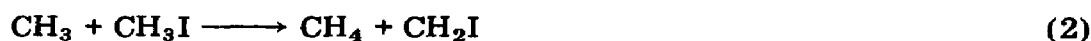
1. Introduction

It is surprising that the photodecomposition products in the iodine laser have received comparatively little attention. In particular, no detailed reports on the products of the CH₃I laser, discovered more than a decade ago by Kasper and Pimentel [2], have been (as far as we know) published. However, the stationary photolysis of CH₃I has been described in considerable detail by West and Schlessinger [3]. The primary process of the photolysis at $\lambda = 253.7$ nm is the dissociation into the radicals CH₃ and I:



The subsequent dark reactions of these radicals are responsible for the complex chemistry observed.

The reaction



*A preliminary communication of some of the data reported in this work has been published [1].

[†]Present address: Department of Chemistry, University of Edinburgh, Gt. Britain.

has been attributed [4] to "hot" CH_3 and some evidence for the reaction



has been given and has subsequently been confirmed [5].

Harris and Willard [6] found enhanced CH_3 radical hydrogen abstraction when the irradiation was performed at 184.9 nm; formation of vibrationally excited CH_3 was the suggested cause. Later work by Souffie *et al.* [7] and by Doepker and Ausloos [8] supported in general terms the previously developed mechanism. An interesting observation is the extremely low quantum yield observed [6] ($\phi \approx 5 \times 10^{-3}$) for a photolysis in which it seems well established that the primary photodecomposition quantum yield is unity. Of course, this result can be easily explained by the combined effect of recombination



and reaction (3).

The development of more sophisticated techniques has allowed a more quantitative approach. Using photofragment spectroscopy Riley and Wilson [9] have unequivocally shown that the "hot" CH_3 formed at $\lambda = 266.2$ nm is predominantly translationally rather than internally excited. Using flash photolysis combined with time-resolved mass spectrometry Rice and Truby [10, 11] have studied the deactivation of CH_3 and conclude that some vibrationally excited CH_3 is formed. Unfortunately the photolysis wavelength responsible for this formation is not certain. Similar techniques have been used to develop a kinetic model and several rate constants have been calculated [12]. The accuracy of this model is, however, questionable. A rate constant for excited iodine deactivation



is reported that seems to be incompatible with more recent work by Butcher *et al.* [13]; they determined accurately the sum of the two excited iodine deactivation rate constants by CH_3I — that of the physical reaction (5) and that of the following chemical reaction:



Most of the recent work on CH_3I photolysis has involved flash techniques. The main purpose of these papers has been to calculate the rate constants of the elementary processes, and very little information has been obtained about the formation of products and the general mechanism of the photolysis [14, 15].

The situation concerning the CH_3I laser is similar; for example, the important phenomenon of laser oscillation quenching has been attributed to an ill-defined "pyrolysis" [16, 17].

In this work we attempt to define more precisely the chemistry of the CH_3I laser based on a detailed analysis of the products formed after laser operation under a variety of conditions. We studied the influences of buffer

gases (SF_6 and argon), the flash energies and the irradiation wavelength. The influence of the chemistry on the laser operation is discussed. It is shown that, by judicious choice of experimental conditions, repetitive operation of the CH_3I laser is possible. The data obtained in this work have helped in the development of a kinetic model for the CH_3I laser [18].

2. Experimental

The central feature of the laser apparatus, which has been described elsewhere [19], was the use of a concentric arrangement of the laser cell, the filter cell and the flash lamp. It was constructed in the following way. A Spectrosil tube (Thermal Syndicate) 67 cm long and of internal diameter 0.75 cm was closed at both ends with microscope cover glasses at the Brewster angle and formed the laser cell for the iodide. A second Spectrosil tube (48 cm \times 1.4 cm) surrounding it formed a second chamber that could be filled with gas or liquid filters. A solution of 4 g l⁻¹ of acetamide in water was used to filter out wavelengths shorter than 220 nm. Without the filter transmission was extended to approximately 165 nm.

An outer Pyrex tube, 40 cm \times 3.2 cm and closed by cylindrical stainless steel electrodes, formed the flash lamp. About 50% of the total volume of the laser cell was illuminated by the flash.

In some of the experiments a similar arrangement, but without the filter chamber, was used. In this case the volume illuminated was 72% of the laser cell.

2.1. Flash characteristics

The capacitor bank (10 μF , Maxwell Series C) was charged with a high voltage power supply up to 20 kV. It was discharged through the lamp with the help of a manual plunger. The risetime of the flash pulse was approximately 10 μs and its full width at half maximum was about 22 μs . The flash was followed using a photodiode (Motorola MRD 500).

The equivalent black-body temperature of the flash lamp was calculated using the equation

$$T = 603 \{j(R - r)^{1/2}\}^{4/11} \quad (7)$$

where j is the current density, and R and r are the outer and inner radii respectively of the flash lamp. Equation (7) is an adaption of the Gusinow equation [20] to the lamps used in this work. Radiated energy distributions at the calculated temperatures were deduced from the standard black-body Planck equation.

2.2. Laser cavity and oscillation

The laser cavity was formed by two spherical gold-coated mirrors of radius 2 m (Laser Optics) placed 1.1 m apart; this gave a stable configuration [21]. The cavity losses were measured to be 29% per "round trip" (*i.e.* a

threshold gain G of 1.4). This figure corresponds to passive cavity losses only; other losses, *e.g.* those caused by optical inhomogeneities in the lasing medium, will increase this value.

A fraction of the laser oscillation was coupled out of one of the Brewster windows and was directed to an indium antimonide IR detector (Mullard, RPY 77).

2.3. Materials and handling

A grease-free vacuum line was used. CH_3I was purified by trap-to-trap distillation prior to its use. The buffer gases (SEO) were used without purification. The mixtures were left overnight before their utilization and were discarded after 48 h.

2.4. Analysis

Qualitative analysis was performed by the gas chromatography-mass spectrometry technique (Pye Unicam-AEI MS 30) using a silica gel column for product separation. Quantitative analysis of CH_3I was performed with gas chromatography (HP 5750) using dinonyl phthalate and thermal conductivity detection; the photolysis products were analysed with a silica gel column and flame ionization detection.

Attempts to analyse molecular iodine failed and were abandoned; irreversible strong iodine absorption by the epoxy resins (Araldite) used in the construction of the cells was unavoidable in the system employed in this work.

3. Results

The analysed products and the experimental conditions (ratios of buffer gases, flash energies etc.) are given in Tables 1 and 2. The initial CH_3I pressure was approximately 6 Torr ($0.328 \times 10^{-3} \text{ mol dm}^{-3}$).

3.1. Experiments with $\lambda > 165 \text{ nm}$

3.1.1. Pure CH_3I

These results are characterized by high decomposition yields and the absence of laser repetitive operation (see Table 1). Because the decomposition increases with increasing energy, the formation of other substances is not included in Table 1. Significant amounts of acetylene at 1100 J were detected but they were not quantitatively analysed. At this energy a significant mass deficit, which is attributed mainly to acetylene formation, is observed.

Obviously under these conditions secondary photolysis of the initial products starts to play a determinant role in the process. The equivalent black-body temperature of the flash increases with energy favouring the formation of more energetic (*i.e.* more reactive) species and, therefore, favouring a more extensive decomposition. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio increases

TABLE 1

Photochemical CH₃I laser with full xenon arc ($\lambda > 165$ nm)

Flash	Energy ^a (J)	Temperature ^b (K) $\times 10^{-3}$	Energy distribution ^c	Products ^d ($\mu\text{mol l}^{-1}$)			Photolysis ^e (%)	Photolysis ^f (%)	CH ₄ /C ₂ H ₆	Number of experiments averaged ^g
				CH ₄	C ₂ H ₆	C ₂ H ₄				
<i>CH₃I pure</i>										
410	9.0		0.21	41.0	13.0	26.0	47.0	41.0	3.1	4
820	10.0		0.28	83.0	5.5	44.0	69.0	64.0	15.0	5
1100	10.6		0.31	85.0	0.71	14.0	73.0	43.0	120.0	5
<i>CH₃I with SF₆ in the ratio 1:9</i>										
500	9.2		0.23	1.7	6.8	1.2	9.8	6.8	0.25	4
820	10.0		0.28	3.4	11.1	2.5	14.6	11.7	0.31	4
1100	10.6		0.31	5.0	13.6	3.5	17.3	14.7	0.36	4
<i>CH₃I with argon in the ratio 1:9</i>										
500	9.2		0.23	4.0	11.0	1.1	10.0	9.7	0.37	3
820	10.0		0.28	21.0	17.0	9.5	25.0	27.0	1.2	2
1100	10.6		0.31	61.0	14.0	31.6	51.0	53.0	4.5	2

^aEnergy discharged.^bCalculated black-body temperature of the flash; see text.^cRatio of the emitted flash energy in the range 165 - 220 nm to that in the range 220 - 350 nm.^dProducts after one shot at the flash energies and initial composition indicated; estimated error 5 - 8%.^eCalculated as $100([\text{CH}_3\text{I}]_i - [\text{CH}_3\text{I}]_f)/[\text{CH}_3\text{I}]_i$; $[\text{CH}_3\text{I}]_i$ is the CH₃I initially introduced into the cell; $[\text{CH}_3\text{I}]_f$ is the CH₃I remaining (analysed by gas chromatography) after the flash.^fCalculated as $100\{[\Sigma P + [\text{CH}_3\text{I}]_f]\}$, where $\Sigma P = \text{CH}_4 + 2(\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4)$.^gThe numbers for the two first mixtures in the cases studied, but not for the last, include experiments with and without laser oscillation. Because there were no observable differences the results were not presented separately.

TABLE 2

Photochemical CH_3I laser with filtered xenon arc ($\lambda > 220 \text{ nm}$)

Flash	Energy ^a (J)	Shots with laser ^b	Total shots ^b	Temperature ^c (K) $\times 10^{-3}$	Energy distribution ^d	Products ^e		10($\text{CH}_4/\text{C}_2\text{H}_6$)	Photolysis ^f (%)	Number of experiments averaged ^g
						CH_4	C_2H_6			
<i>CH₃I pure</i>										
540	1	1	1	8.0	0.16	0.25	6.3	0.40	3.4	2
540	3	3	3	8.0	0.16	0.56	16.7	0.34	8.7	2
540	23	24	24	8.0	0.16	7.8	127.0	0.61	62.0	1
<i>CH₃I with SF₆ in the ratio 1:9</i>										
540	1	1	1	8.0	0.16	0.06	2.0	0.30	1.3	3
1200	2	3	3	9.2	0.23	0.16	20.0	0.08	12.0	2
<i>CH₃I with argon in the ratio 1:9</i>										
540	1	1	1	8.0	0.16	0.036	4.2	0.086	2.5	3
540	1	2	2	8.0	0.16	0.050	7.3	0.068	4.4	2
1200	2	3	3	9.2	0.23	0.34 ^h	27.3	0.088	16.5	1

^aEnergy discharged.^bNumber of flashes on a given sample that resulted in laser oscillation and total before analysis.^cCalculated black-body temperature of the flash.^dRatio of flash energy in the range 165 - 220 nm to that in the range 220 - 350 nm.^eProducts found after the number of shots at the flash energies and initial composition indicated; traces of C_2H_4 were found in the experiments with CH_3I pure.^fCalculated as $100 \{ \Sigma P / (\Sigma P + [\text{CH}_3\text{I}]_f) \}$, where $\Sigma P = \text{CH}_4 + 2\text{C}_2\text{H}_6$ and $[\text{CH}_3\text{I}]_f$ is the undecomposed CH_3I .^gAll experiments with laser oscillation, except the last of a given series (i.e. of the 24 shots reported at 540 J with CH_3I pure, the first 23 were with laser oscillation, but the 24th was without).^hBecause of an experimental failure this figure has a 100% error.

dramatically with flash energy, indicating significant changes in the photochemical process.

3.1.2. $\text{CH}_3\text{I-SF}_6$ in the ratio 1:9 at $\lambda > 165 \text{ nm}$

These results are characterized by a drastic reduction in the percentage of photodecomposition products compared with those for pure CH_3I (Table 1). Except for acetylene, the products observed were the same as those in the experiments without buffer gas.

However, the relative percentage photolysis increases with energy in a similar way to that for pure CH_3I , although the increase is slightly reduced and the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio is much less sensitive to the flash energy.

Repetitive operation was found — 4, 3 and 2 consecutive laser oscillations on a given mixture were observed at 500, 820 and 1100 J respectively.

3.1.3. $\text{CH}_3\text{I-argon}$ in the ratio 1:9 at $\lambda > 165 \text{ nm}$

The products found were the same as those when SF_6 was used as the buffer gas (Table 1). However, the percentage of photodecomposition is higher; it is intermediate between the pure CH_3I and $\text{CH}_3\text{I-SF}_6$ cases. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio also shows an intermediate behaviour. No laser repetitive operation was observed.

3.2. Experiments with $\lambda > 220 \text{ nm}$

The most obvious effect of the filtering out of wavelengths below 220 nm is a dramatic decrease in the photodecomposition (Table 2). The highest percentage of photolysis per shot is about 5% ($\text{CH}_3\text{I-Ar}$ at 1200 J), which is lower than the lowest decomposition ($\approx 7\%$) with the full xenon arc (1:9 $\text{CH}_3\text{I-SF}_6$ at 500 J).

There is a significant difference between the experiments with and without buffer gas. The decomposition is greater by a factor of about 15 for the CH_3I experiments at a similar flash energy but without a filter. This factor is reduced by the buffer gases to approximately 5. The increased photolysis at short wavelengths may be attributed to the following factors.

(1) The increase of the number of photons absorbed by the CH_3I is caused by the high extinction coefficient of CH_3I below 220 nm [22].

(2) Because the absorbed photons have higher energy, they are able to populate highly excited states initially. These states are capable of inducing a substantial amount of secondary (*i.e.* chemical) decomposition of the CH_3I . We will come back to these points later.

The effect of the elimination of short wavelengths on the distribution of products should also be noted. The traces of acetylene disappear. Ethylene is practically eliminated; although some vestiges are found without buffer gases, it is quantitatively measurable only after 24 flashes. The quantity of methane is also drastically reduced. The buffer gases intensify these tendencies. Thus, under these conditions ethane and presumably molecular iodine (not analysed but visually observed) are the main photolysis products.

However, the most remarkable effect of the wavelength cut off is on laser repetitive operation. For 23 successive flashes of 540 J on 6 Torr of CH_3I there was successful and gradually decreasing laser oscillation. The 24th shot failed. Argon and SF_6 substantially deteriorate this repetitive operation. It was not observed at a flash energy of 540 J. In both cases a maximum of two consecutive lasers was obtained with an increase of the energy to 1200 J.

4. Discussion

4.1. Vibrational versus translational excitation

We will describe some of the energy transfer properties of SF_6 and argon, since this information is required for a discussion of "hot" CH_3 deactivation.

A simple approach [10], that takes into account both collision frequency and kinetic energy transfer, gives a ratio $k(\text{Ar})/k(\text{SF}_6)$ of the deactivation rate constants for translationally hot CH_3 by argon and SF_6 . In contrast, namely 1.8. However, SF_6 is considered to be a much faster vibrational deactivator than argon, because in SF_6 $\text{V} \rightarrow \text{V}$ transfer can occur whilst in argon only the slower $\text{V} \rightarrow \text{T}$ energy transfer can take place [23], *i.e.* the ability of argon as a translational deactivator is twice that of SF_6 . In contrast, SF_6 could be up to 10^3 times faster in removing vibrational energy than argon (this value applies to resonant transfer; non-resonant transfer, which occurs in these experiments, can be one or two orders of magnitude slower).

In Section 3.2 the extensive decomposition found in the experiments without light filter ($\lambda > 165$ nm) was attributed to two factors. The first factor is the increase in the quantity of flash light absorbed by CH_3I ; the second is an increase in the photodecomposition quantum yield. This occurs because the initial fragments have greater energy, they are thus more reactive and consequently the secondary dark reactions increase.

Unless otherwise stated the experiments at lower energy, *i.e.* at 500 J, will be referred to in the following discussion. Although the trends are the same for all the experiments, the product photolysis participation somewhat obscures the results at higher energies (Table 1).

The aforementioned second factor has been attributed to the formation of vibrationally "hot" CH_3 at shorter wavelengths [5]. The production of this radical can be used to explain the dramatic decrease in decomposition when buffer gases are present. Photodecomposition in the experiments at $\lambda > 165$ nm is reduced by a factor of about 6 by SF_6 and of about 4 by argon. The greater effect of the vibrational SF_6 deactivator over the translational argon deactivator is in agreement with our earlier hypothesis. The ratio of the abstraction reaction (2), a reaction which is characteristic of vibrationally excited CH_3 , to CH_3 recombination, a "cold" reaction, should be related to the ratio $\text{CH}_4/\text{C}_2\text{H}_6$ (see Table 1). This ratio decreases in the

order $\text{CH}_3\text{I} \gg \text{CH}_3\text{I-Ar} > \text{CH}_3\text{I-SF}_6$, as expected for a vibrationally "hot" radical.

The moderation effect of SF_6 has a repercussion on laser oscillation. Thus, in the presence of 54 Torr of SF_6 , repetitive laser oscillation on a given mixture was observed, *i.e.* a maximum of four consecutive lasers at the lowest energy, decreasing to two at the highest. Under similar conditions no repetitive operation was obtained with argon or without buffer gas. The improved laser performance is attributed to the vibrational deactivation of CH_3 by SF_6 .

In the experiments where a filter was used (*i.e.* at $\lambda > 220$ nm) the photodecomposition trends are similar but lessened; SF_6 reduces decomposition by a factor of 2.6 and argon by only a factor of 1.4. However, the ratio $\text{CH}_4/\text{C}_2\text{H}_6$ does not follow the same pattern; the ratios at 540 J decrease in the order $\text{CH}_3\text{I} > \text{CH}_3\text{I-SF}_6 > \text{CH}_3\text{I-Ar}$.

However, it is questionable whether this order is maintained at higher energies, where argon and SF_6 seem to have very similar effects on the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio. These results contradict somewhat the decomposition results. Although argon is a better CH_3 translational deactivator than SF_6 , it is not, as seen in the ratio comparison, a better buffer gas from the decomposition point of view. This result, which is not surprising, indicates that decomposition via hot radicals is probably not predominant. Both the concentration and the energy of the CH_3 radicals formed at $\lambda > 220$ nm should be smaller than those for the radicals formed at $\lambda > 165$ nm. Therefore their participation in secondary decomposition should also not be very important and other mechanisms will occur under these conditions.

4.2. Repetitive laser operation and gain

More evidence for a change in the mechanism with wavelength is provided by observations on laser repetitive operation. If the relationship between decomposition and repetitive operation (*i.e.* the more decomposition, the less favourable is laser repetition) obtained in the experiments without filter are to be maintained with filter, we would expect that, in this case, operation with SF_6 would sustain repetitive operation most effectively, followed by argon. In fact the opposite was found; 23 consecutive lasers were observed without buffer gas and no repetitive operation was observed with SF_6 or argon.

However, if we had taken into account the requirements for laser oscillation, these results would have been easily explainable and even predictable. In order to emit a laser has to overcome the gain threshold due to cavity losses. But, in repetitive operation (*i.e.* in laser consecutive operation on a given mixture), some quenchers are formed after the first shot as a consequence of the photolysis induced by the flashes. Therefore in order to lase the system has to overcome these additional "chemical losses" introduced into the system, *i.e.* the threshold gain must increase after the first shot.

The laser small signal gain G where

$$\ln G = \sigma \Delta N L$$

(8)

can be used to discuss this problem. This equation, where L is the length of the active medium, relates the gain to the product of the cross section σ of stimulated emission and the population inversion ΔN . We are now in a position to explain repetitive operation, or the lack of it, in terms of σ and ΔN .

The presence of buffer gases reduces the value of σ by collisional broadening to less than one half of its value in pure CH_3I [24]. This gain loss is partially compensated for by an increase in ΔN because of buffer moderator effects [18]. The net result is that the gain is slightly higher for pure $\text{CH}_3\text{I}^\dagger$. However, this quantitatively small difference may be significant if the laser oscillates at gains very close to the threshold (see Section 2.2). Thus the initial drop in gain after the first shot, which should be more marked than that in subsequent shots [25], is enough to prevent laser repetition in the argon and SF_6 experiments.

To verify this point we increased the gain using a more energetic flash so that the population inversion increased. As expected we obtained laser repetitive operation (see Table 2), but only up to two consecutive lasers; this result is in agreement with the small gain differences observed. Obviously, although our argument is qualitatively correct, some additional mechanism is operating in the same direction (see Section 4.3).

4.3. Molecular iodine quenching

We attribute the limitation effect on laser repetition to the fast I_2 quenching of I^* ; it is masked by decomposition and secondary quenching in the experiments at $\lambda > 165$ nm. The remaining question is why this I_2 seems not to affect the laser operation of pure CH_3I at $\lambda > 220$ nm where repetitive lasers are obtained at decompositions of approximately 55%, whereas the mixtures with buffer gases are unable to operate even at much higher flash power. Attempts to obtain laser oscillation at $\lambda > 220$ nm with buffer gases at 1200 J fail when the decomposition is about 10%. The formation of I_2 in the different cases should not be very different, *i.e.* a fast formation by reaction (6) and a slow recombination of atomic iodine. If, according to this argument, the decomposition gives an indication of the I_2 formed, then the pure CH_3I at 500 J laser, with a gain well below that of $\text{CH}_3\text{I-SF}_6$ at 1200 J, should be able to maintain laser oscillation at an I_2 concentration about 5 times higher. This is obviously impossible. The answer to this paradox is that the implied assumption that all the I_2 formed remains in the gas phase and can act as quencher is erroneous.

Calculation of the diffusion coefficients [26] for I_2 in CH_3I (6 Torr) and in $\text{CH}_3\text{I-SF}_6$ (1:9 ratio, 60 Torr total pressure) yields a coefficient 10 times greater in the former case. According to our calculations, (see Fig. 1 and the appendix), in pure CH_3I the I_2 has enough time between shots to

[†] The results given in ref. 1 were revised and we found $G(\text{CH}_3\text{I}, 540 \text{ J}) = 1.8 \pm 0.1$, $G(\text{CH}_3\text{I-Ar}, 540 \text{ J}) = G(\text{CH}_3\text{I-SF}_6, 540 \text{ J}) = 1.7 \pm 0.1$ and $G(\text{CH}_3\text{I-SF}_6, 1200 \text{ J}) = 2.0$. The minimum threshold gain was 1.4 (see Section 2.2). These data are applicable to the conditions used in this work.

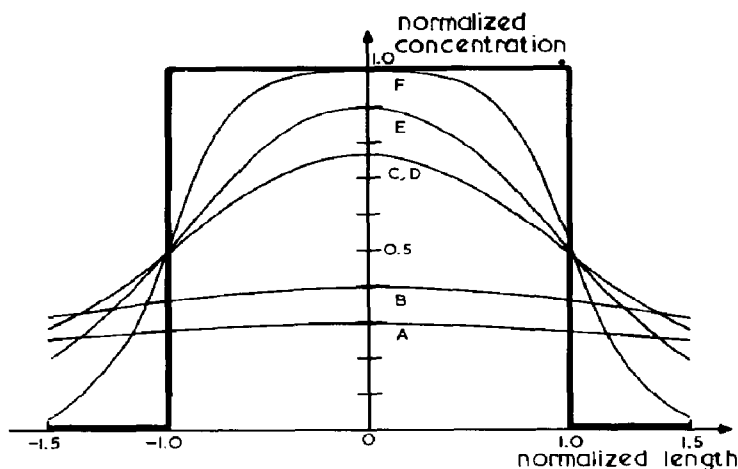


Fig. 1. Longitudinal concentration distributions of I_2 in the laser cell after photolysis at various times. The initial concentration at $t = 0$ for a laser cell normalized length from -1 to $+1$ is given by the heavy line. Curves A, B and C are for I_2 in pure CH_3I at 600, 300 and 60 s respectively. Curves D, E and F are for I_2 in CH_3I-SF_6 (1:9) at 600, 300 and 60 s respectively. The minimum time interval between shots in real experiments (repetitive operation) was $t \geq 300$ s.

migrate to the extremes of the plasma cell and remain there; some of the I_2 covers the walls out of the range of the flash and some is absorbed by the epoxy resin that cements the Brewster windows*. However, the transport of I_2 in the presence of SF_6 (or argon) is slower and the I_2 can exercise its powerful quenching effect in subsequent flashes. This argument is confirmed by visual inspection of the laser cell. With CH_3I at 540 J two flashes are enough for the I_2 to be noticeable at the laser cell end. After 23 lasers the wall at the ends of the cell out of the flash range is reddish in colour and the epoxy resin is totally black. In the presence of SF_6 after two lasers at 1200 J no I_2 is visible at the ends. Thus, under these conditions, diffusion of I_2 to the cell ends is not fast enough and the iodine is forced to remain in the gas phase.

5. Conclusions

We conclude that the CH_3I laser can be operated under conditions of decomposition which are very close to those of CF_3I for example, but at a reduced gain because of the strong quenching by the substrate (reactions (5) and (6)). This similar behaviour at reduced gain could be of interest in a detailed study of the influence of diverse parameters on the iodine laser under conditions where the system is very sensitive to minute changes.

*This strong irreversible absorption by epoxy resins is well known for I_2 in the gas phase.

From the photochemical point of view the predominant formation of vibrationally hot methyl radical at $\lambda < 220$ nm and of translationally excited methyl at $\lambda > 220$ nm is confirmed.

From the laser point of view the increased gain with $\lambda > 165$ nm relative to experiments at $\lambda > 220$ nm is evident. The repetitive operation found with $\text{CH}_3\text{I-SF}_6$ at 540 J without filter can be compared with the lack of repetition with filter under the same conditions. This result indicates that photolysis of CH_3I at short wavelengths ($\lambda < 220$ nm) contributes to the formation of population inversion and therefore to the formation of $\text{I}(5^2\text{P}_{1/2})$.

The qualitative arguments described in this work have been used quantitatively to develop a kinetic model of the CH_3I laser that appears to predict the laser behaviour satisfactorily [18].

Acknowledgments

We thank Professor Roberto M. Utrilla and Dr. Vicente Menéndez for many helpful discussions. A. C. and M. M. held Fellowships from the C.S.I.C., and L. V. held a Fellowship from the Instituto Español de Emigración and Fundación Santa María. This research was partially supported by grant 1305 of Comisión Asesora de Investigación Científica y Técnica.

References

- 1 A. Costela, J. M. Figuera, M. Martín and L. Valle, *Chem. Phys. Lett.*, **58** (1978) 478.
- 2 J. V. V. Kasper and G. C. Pimentel, *Appl. Phys. Lett.*, **5** (1964) 231.
- 3 W. West and L. Schlessinger, *J. Am. Chem. Soc.*, **60** (1938) 961.
- 4 R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18** (1950) 194.
- 5 N. Davidson and T. Carrington, *J. Am. Chem. Soc.*, **74** (1952) 6277.
- 6 G. M. Harris and J. E. Willard, *J. Am. Chem. Soc.*, **76** (1954) 4678.
- 7 R. D. Souffie, R. R. Williams and W. H. Hamill, *J. Am. Chem. Soc.*, **78** (1956) 917.
- 8 R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **41** (1964) 1865.
- 9 S. J. Riley and K. R. Wilson, *Discuss. Faraday Soc.*, **53** (1972) 132.
- 10 J. M. Rice and F. K. Truby, *Chem. Phys. Lett.*, **19** (1973) 440.
- 11 J. M. Rice and F. K. Truby, *Int. J. Chem. Kinet.*, **9** (1977) 693.
- 12 D. M. Haaland and R. T. Meyer, *Int. J. Chem. Kinet.*, **6** (1974) 297.
- 13 R. J. Butcher, R. J. Donovan, C. Fotakis, D. Fernie and A. G. A. Rae, *Chem. Phys. Lett.*, **30** (1975) 398, and references cited therein.
- 14 V. Yu. Zalesskii, *Sov. J. Quantum Electron.*, **4** (1975) 1009.
- 15 R. E. Palmer and T. D. Padrick, *J. Chem. Phys.*, **64** (1976) 2051.
- 16 V. Yu. Zalesskii and E. J. Moskalev, *Sov. Phys. — JETP*, **30** (1970) 1019.
- 17 E. V. Arkhipova, B. L. Borovich and A. K. Zapol'skii, *Sov. J. Quantum Electron.*, **6** (1976) 686.
- 18 A. Costela, J. M. Figuera, M. Martín, J. M. Pérez and L. Valle, *J. Chem. Soc., Faraday Trans. II*, in the press.
- 19 A. Costela, J. M. Figuera and J. M. Pérez, *An. Quim.*, **73** (1977) 1521.
- 20 M. A. Gusinow, *J. Appl. Phys.*, **44** (1973) 4567.

- 21 M. J. Beesley *Lasers and their Applications*, Taylor and Francis, London, 1972.
 22 R. A. Boschi and D. R. Salahub, *Mol. Phys.*, **24** (1972) 289.
 23 K. L. Kompa, *Fortschr. Chem. Forsch.*, **37** (1973) 1.
 24 W. Fuss and K. Hohla, *Z. Naturforsch., Teil A*, **31** (1976) 569.
 25 C. C. Davis, R. J. Pinkle, R. A. McFarlane and G. J. Wolga, *IEEE J. Quantum Electron.*, **12** (1976) 334.
 26 W. Kauzmann, *Kinetic Theory of Gases*, Benjamin, New York, 1966, p. 203.

Appendix

Molecular iodine diffusional mixing [25]

The distribution of iodine molecules in the photolysis tube as a function of time, normalized to an initial unit I_2 concentration of uniform density from $x = -1$ to $x = +1$, is given by

$$[A] = \frac{1}{2} [A_0] \left[\operatorname{erf} \left\{ \frac{1-x}{2(Dt)^{1/2}} \right\} + \operatorname{erf} \left\{ \frac{1+x}{2(Dt)^{1/2}} \right\} \right] \quad (\text{A1})$$

where D is the diffusion coefficient.

The calculated coefficients [26] were $D(I_2-CH_3I) = 2.31 \text{ cm}^2 \text{ s}^{-1}$ and $D(I_2-CH_3I + SF_6) = 0.24 \text{ cm}^2 \text{ s}^{-1}$. The results obtained from eqn. (A1) for these parameters are plotted in Fig. 1.