465

A REVIEW OF STUDIES INVESTIGATING A POTENTIAL CHEMICAL LASER PUMPING SCHEME: IF(B $^3\Pi(0^+)$) PUMPING BY ENERGY TRANSFER FROM O$_2$($^1\Delta$) TO IF(X $^1\Sigma^+$)[†]

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Summary

In this paper results obtained from studies related to a potential chemical laser based on the B–X transitions of iodine monofluoride (IF) are reviewed. The paper includes a summary and discussion of the optically pumped IF laser studies of Davis *et al.* with particular emphasis on how these results impact the potential IF chemical laser. The paper will also provide a summary and discussion of the kinetic and mechanistic studies reported to date on O$_2$($^1\Delta$) energy transfer to IF.
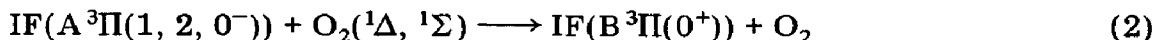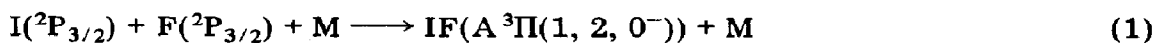
1. Introduction

Chemiluminescent processes resulting from energy transfer reactions of O$_2$($^1\Delta$) with diatomic species such as I$_2$, Br$_2$, IF, BrF, S$_2$ and SO have been reported [1 - 4]. The dissociation of I$_2$ and subsequent electronic excitation of iodine atoms [1] has received much attention in the last 5 years because it is the basis of the chemical oxygen–iodine laser [5 - 7]. Derwent and Thrush [1] were the first to propose a chemical laser based on these energy transfer reactions. The successful demonstration of lasing on the I(^{2}P$_{1/2}$) $\rightarrow$ I(^{2}P$_{3/2}$) spin–orbit transitions of atomic iodine was dependent on the development of a high yield chemical generation system for O$_2$($^1\Delta$) [8]. This generator utilized the heterogeneous reaction of chlorine gas with concentrated basic hydrogen peroxide [9, 10]. The advent of an efficient O$_2$($^1\Delta$) chemical generator has led to other chemiluminescent processes depending on O$_2$($^1\Delta$) energy transfer being considered as potential chemical lasers.
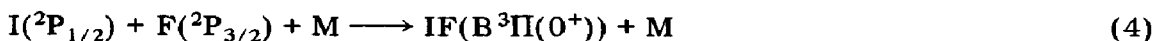
Recent work on the measurement of the kinetics and laser spectroscopy of fluorine–iodine mixtures [11 - 19] has led to the proposal of a continuous wave visible chemical laser operating on the B–X transitions of IF [11].

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In such a laser, the population inversion would be provided by energy transfer from $O_2(^1\Delta)$ to IF generated in the reactive flow of I_2 and F_2. The concept of the IF chemical laser arose from the correlation of two separate studies by Clyne and coworkers [3, 13 - 15]. Clyne and McDermid [13 - 15], in a series of high resolution time-resolved laser-induced fluorescence experiments, have made an extensive study of the energy levels and radiative dynamics of the $IF(B^3\Pi(0^+))$ state. From this work they concluded that the B–X transitions would be suitable candidates on which to attempt to develop an optically pumped laser [15]. In a study prior to that just described, Clyne *et al.* [3] reported intense IF(B–X) chemiluminescence when the following gas mixture was established in a flow reactor: F–F_2, I–I_2 and the products of a microwave discharge in O_2 from which oxygen atoms had been removed with a mercury oxide coating. The chemiluminescence was attributed to energy transfer from either $O_2(^1\Delta)$ or $O_2(^1\Sigma)$ via either of these mechanisms:

$$I(^2P_{3/2}) + F(^2P_{3/2}) + M \longrightarrow IF(A^3\Pi(1, 2, 0^-)) + M \tag{1}$$

$$IF(A^3\Pi(1, 2, 0^-)) + O_2(^1\Delta, {}^1\Sigma) \longrightarrow IF(B^3\Pi(0^+)) + O_2 \tag{2}$$

or

$$I(^2P_{3/2}) + O_2(^1\Delta) \longrightarrow I(^2P_{1/2}) + O_2 \tag{3}$$

$$I(^2P_{1/2}) + F(^2P_{3/2}) + M \longrightarrow IF(B^3\Pi(0^+)) + M \tag{4}$$

Thus the following question arises: if the IF(B–X) transitions will support lasing, could the high yield chemical $O_2(^1\Delta)$ generator technology be employed to provide the chemical pump for a high energy IF(B–X) chemical laser?

2. The optically pumped IF(B–X) laser

The $B^3\Pi(0^+)$ state of IF has a much greater equilibrium internuclear separation than that of the $X^1\Sigma^+$ state. Hence, the B–X transitions with the highest Franck–Condon factors are those from low B(v') levels to X($v'' > 0$) levels (*e.g.* (0, 4) (0, 5) (0, 6) (2, 10) (3, 11)). Such a situation favors the formation of a population inversion on these transitions, particularly at room temperature where the Boltzmann population distribution for $v'' > 0$ will be considerably less than that for $v'' = 0$. Davis and Hanko [16] utilized the slow reaction between I_2 and F_2

$$I_2 + F_2 \longrightarrow I_2F + F \tag{5}$$

$$I_2F + F \longrightarrow 2IF \tag{6}$$

to produce IF(X) in high yield. This scheme was first proposed by Valentini and coworkers [20, 21]. The overall rate constant for $I_2 + F_2 \rightarrow$ products was

measured by Whitefield and Davis [11] to be $(1.9 \pm 0.3) \times 10^{-15}$ cm^3 s^{-1}. This is a reactively slow, but straightforward, technique for producing IF(X). Reaction (5) has an activation barrier of about 17 kJ mol^{-1} [21]. Reaction (6), however, is considerably exoergic (-267 kJ mol^{-1}) and thus a proportion of the IF product is found to be electronically excited in the B state.

With this method for producing IF(X), Davis and Hanko [16] first reported an optically pumped IF laser in 1980. The optical pumping was achieved with a high energy broad band pulsed dye laser. They reported lasing from pumped levels in the IF(B) state on transitions with high Franck–Condon factors $(v', v'') = (2, 10)$, $(3, 11)$, $(4, 9)$ and $(4, 10)$. In a subsequent publication a more detailed optical pumping study was reported [17]. Pulsed lasing was observed from the pumped vibrational levels $v' = 1$ - $v' = 6$. At longer time intervals after the pump pulse, lasing was also observed from vibrational levels lower than those pumped. This effect has been explained by rapid vibrational thermalization in the B state, which is brought about by collisions with the diluent gas. The time interval between the pump pulse and the thermalized lasing pulse was observed to decrease with increased carrier gas pressure $P < 26$ kPa. Pumped level lasing terminated at a carrier gas pressure $P > 1.1$ kPa.

Thermalized lasing was also found to be efficient; a comparison of the pump pulse energy with that of the thermalized laser output revealed an efficiency of 1.5%. Thermalized lasing at laser cavity pressures up to 26 kPa suggests that the system would survive the higher pressure regime most likely required for a scaled-up chemical device. Also in a chemically pumped system, e.g. energy transfer from $O_2(^1\Delta)$, the transferred chemical energy would be expected to be distributed over several levels of the B state vibrational manifold (see below). The capability for thermalized lasing indicates that most of the available energy distributed chemically into the B state manifold could be channeled into $v' = 0$ prior to lasing, thus enhancing the population inversion ratio.

3. Chemical pumping with $O_2(^1\Delta)$

The chemical pumping studies reported to date [3, 12, 18, 22] have dealt largely with examinations of the various chemiluminescent energy transfer processes producing IF(B–X) emission (i.e. $O_2(^1\Delta) + IF$, $O_2F + I_2$, $NF(^1\Sigma) + IF$). Following the phenomenological report by Clyne et al. [3] where the true source of excitation was not established (they inferred from their observations that the pumping depended on the termolecular processes (reactions (1) - (4)), Whitefield et al. [12] have reported studies of the IF(B–X) emission arising from three groups of reagents: (a) $F_2 + I_2$, (b) $F_2 + I_2 + O_2(^1\Delta)$ and (c) $F-F_2 + I_2 + O_2(^1\Delta)$. The emission was found to be strongly dependent on the composition of the reactant mixture and the type of mixing. In Fig. 1 are typical spectra for reagent groups (a) and (c)
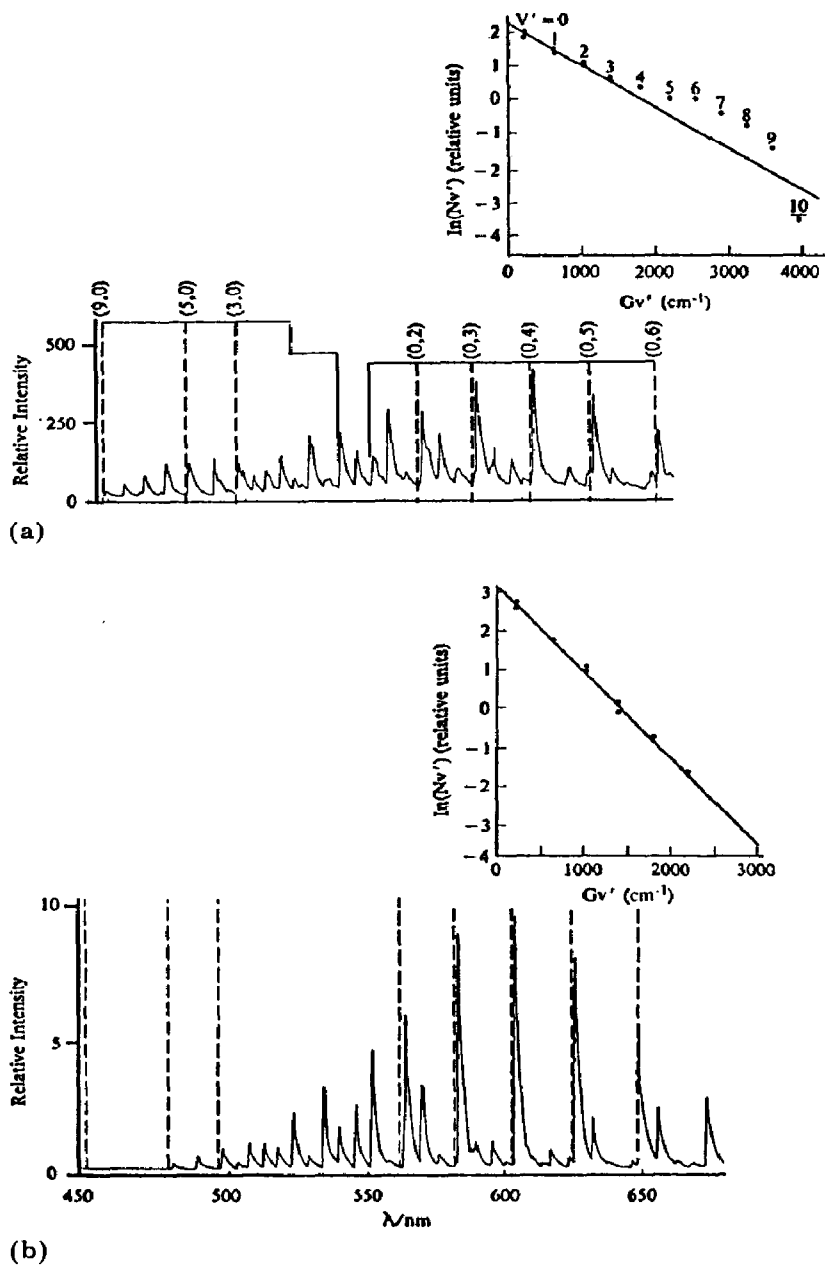
468

(a)

(b)

Fig. 1. Comparative spectra and vibrational population distributions for the IF(B–X) flames produced from reactant groups (a) $F-F_2 + I_2 + O_2(^1\Delta)$ (O_2 pressure, 133 Pa (5% of which is $O_2(^1\Delta)$); F_2 pressure, 40 Pa ([F]:[F_2] unknown); I_2 pressure, 4 Pa; helium pressure, 56 Pa; total pressure, 233 Pa) and (b) $F_2 + I_2$ (helium pressure, 213 Pa; F_2 pressure, 49 Pa; I_2 pressure, 4 Pa; total pressure, 266 Pa).

obtained under given reaction conditions. Figure 1 also includes plots of vibrational population distributions calculated for both spectra. The spectrum in Fig. 1(b) is that obtained when I_2 and F_2 react. It is a typical low resolution chemiluminescence spectrum of the IF(B–X) system with strong

emission from $v' = 0$. On the addition of microwave-discharged O_2 (where the oxygen atoms were removed and about 5% of the O_2 flow was $O_2(^1\Delta)$) at a pressure of 70 Pa, the emission intensity was enhanced by an order of magnitude. The addition of fluorine atoms, accompanied with simultaneous mixing of all three reagents, produced approximately a fiftyfold intensity enhancement of the IF(B–X) luminescence compared with that produced by the $I_2 + F_2$ reaction. The luminescence spectra from reagent schemes (b) and (c) not only demonstrated an intensity enhancement, but also demonstrated that the relative emission from hot bands ($v' > 0$) was much greater when $O_2(^1\Delta)$ was present.

The spectrum in Fig. 1(a) is that for a typical $F-F_2 + I_2 + O_2(^1\Delta)$ flame. There is an anomalously high population distribution in the vibrational levels $v' = 5 - v' = 9$. Considering only the vibrational levels $v' = 0 - v' = 4$ for this flame, the calculated populations have thermal distributions for vibrational temperatures in the range from 800 to 1100 K. Emission from $v' \geqslant 10$ was not observed in the chemiluminescence spectra since predissociation is predominant for $v' > 9$ [15]. The anomalous populations of $v' = 5 - v' = 9$ at low total pressures for the $F-F_2 + I_2 + O_2(^1\Delta)$ flames indicate preferential pumping of these levels by $O_2(^1\Delta)$.

The flame arising from the simultaneous mixing of $F-F_2 + I_2 + O_2(^1\Delta)$ has two distinct regions. The first, beginning at the I_2 injector, is extremely intense and persists downstream for about 10 ms. This region was readily extinguished by moving the I_2 injector either upstream or downstream from the simultaneous mixing plane (thus destroying the simultaneous mixing situation). Such a flame indicates direct reactions occurring between $F-F_2$, I_2 and $O_2(^1\Delta)$.

The second region filled the entire flow reactor and was similar to that described by Clyne *et al.* [3], who reported a chemiluminescence from IF with the visual appearance of the N_2 afterglow produced from radiative recombination of $N(^4S)$ atoms. As previously indicated, Clyne *et al.* attributed this emission to reactions such as reactions (2) - (4). This type of emission was the only emission observed when simultaneous mixing was destroyed. High population in the $v' = 5 - v' = 9$ levels provides an opportunity for collisional promotion of IF molecules into the unstable predissociation region of the B state manifold. Such collisional promotion will cause non-radiative loss of excited IF in the direct excitation region of the $F-F_2 + I_2 + O_2(^1\Delta)$ flame. Collisional promotion of IF into the predissociation region of the B state manifold may, in part, be responsible for the diffuse flame (second flame region). The products of this predissociation will be $I(^2P_{1/2})$ and $F(^2P_{3/2})$ atoms. These species can radiatively recombine and generate IF(B–X) emission as in reactions (1) - (4).

Predissociation as a result of collisional ladder climbing has been observed in other interhalogens [23, 24]. A maximum photon yield measurement has been made for the $F-F_2 + I_2 + O_2(^1\Delta)$ flame of 0.3%, measured as the ratio of the IF(B) photons detected per second to the I_2 molecules consumed per second. This yield is surprisingly low, and may be explained

in part by the collisional promotion described above. The extent to which this collisional promotion or ladder climbing occurs must be examined since, if it proves to be a significant non-radiative loss process, the extent to which it occurs will have to be included in any scaling modeling for the device.

Whitefield *et al.* [12] also measured the rotational temperature of the 0—5 band over a wide range of flame conditions and found that, in the pressure range from 0.07 to 0.3 kPa, the rotational temperature was 315 ± 15 K. Furthermore, no systematic trends with total pressure or reagent partial pressure were observed. Thus rapid rotational—translational transfer processes occur in the IF(B) state where rotational thermalization is complete within an IF(B) lifetime for carrier gas pressures as low as 0.07 kPa.

4. Mechanisms for $O_2(^1\Delta)$ pumping IF

With the information from the chemiluminescence data and other available rate data, it is possible to propose two empirical mechanisms for $O_2(^1\Delta)$ pumping of IF (Fig. 2). In the mechanistic discussion to follow, all reactions are referred to by their identifying letter (*i.e.* reactions (A) - (J) as shown in Fig. 2). To promote IF(X) $v'' = 0$ to the IF(B) state requires a minimum of about $18\,950$ cm^{-1} ($v(0, 0) = 18\,952$ cm^{-1}), which is equivalent to about 2.5 $O_2(^1\Delta)$ quanta [25]; thus $O_2(^1\Delta)$ pumping IF is not a single-step energy transfer process. The rate constant k for the F + I$_2$ reaction has been measured [26] as $(4.3 \pm 1.1) \times 10^{-10}$ cm^3 s^{-1}. Such a large rate constant makes the F + I$_2$ reaction the most likely initiation step in any pumping mechanism for the F–F$_2$ + I$_2$ + $O_2(^1\Delta)$ flame. The reaction is also exothermic by 9897 cm^{-1}. There is some controversy as to whether a significant portion of this exothermicity is released as either electronic excitation of the atomic iodine or vibrational excitation of the IF(X) product (reactions (A) and (B)) [27 - 30]. Nevertheless, the production of iodine atoms in the presence of $O_2(^1\Delta)$ will result in their electronic excitation (reaction (C)) [1]. This being the case, the products of reactions (E) and (F), I(^{2}P$_{3/2}$) + F$_2$ and I(^{2}P$_{1/2}$) + F$_2$ respectively, are of interest. Reaction (F) is exothermic by $17\,900$ cm^{-1} which is sufficient energy for the IF product to be electronically excited into A $^3\Pi(n)$ states.

The A $^3\Pi(n)$ states of interest are the A $^3\Pi(1)$ and A $^3\Pi(2)$ states. The A $^3\Pi(1)$ state has been assigned ($v(0, 0) = 15\,591$ cm^{-1}) [25]. The A $^3\Pi(2)$ state has not been directly observed but has been suggested as the terminating level of the electrically pumped IF(D$'$–A$'$) laser [31, 32]. These states lie below the B $^3\Pi(0^+)$ state in energy. Alternatively, the IF is produced in the IF(X) state with extremely high vibrational excitation, typically $v'' \leqslant 28$. High resolution, rotationally resolved, spectra of the F–F$_2$ + I$_2$ + $O_2(^1\Delta)$ flame revealed no signs of IF(A–X) emission. The absence of IF(Δ–X) emission is not surprising, however, since only a low steady state, IF(A $^3\Pi(n)$), would be expected if the IF(A $^3\Pi(n)$) species were an
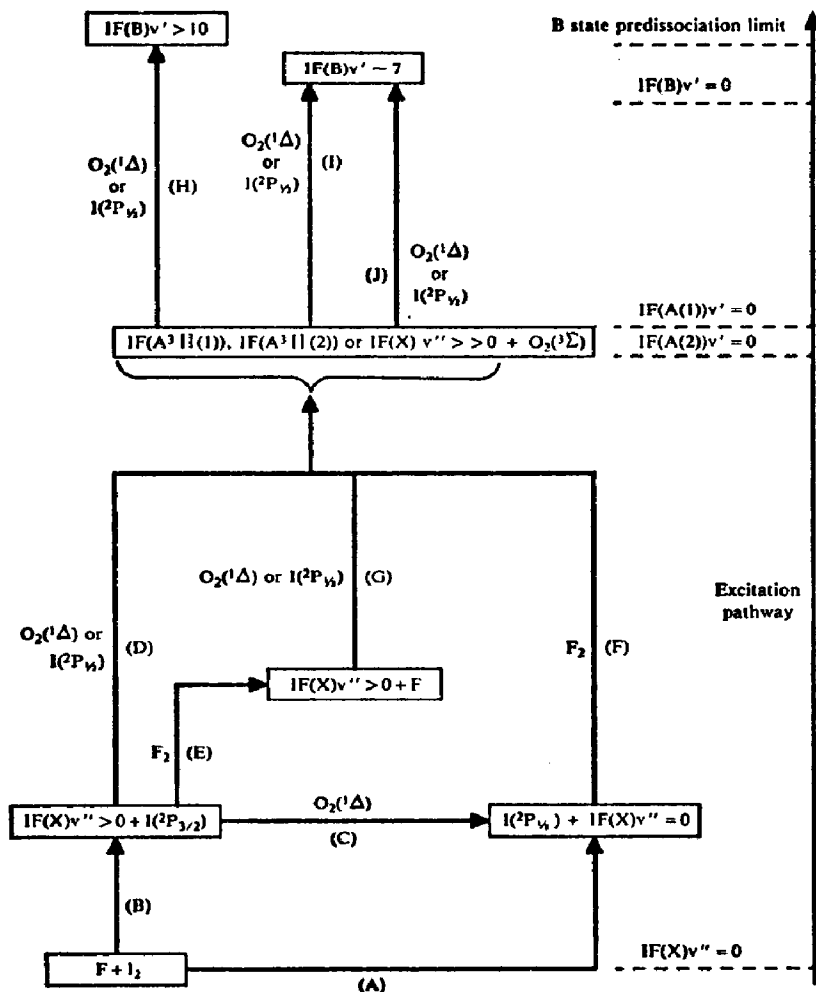
Fig. 2. Overall reaction chart for potential IF(B) pumping schemes (the reactions are lettered to be consistent with the text).

intermediate in an efficient IF(B) pumping process, as could be the case of reactions (D), (F) and (G) with (H) and (I). If reactions (H) - (J), the second stage for IF(B) pumping by $O_2(^1\Delta)$, are resonant energy transfer reactions, one $O_2(^1\Delta)$ quantum would pump IF($A^3\Pi(1)$) molecules beyond the predissociation limit in the $B^3\Pi(0^+)$ state, as shown in reaction (H). Such pumping would result in non-radiative loss of IF(B) and subsequently reduce the efficiency of the IF(B) photon production measured as described above.

For IF($A^3\Pi(2)$) as the molecular product of reaction (F), an estimate of the energy of the $A^3\Pi(2)$ state can be calculated from the IF($D'-A'$) laser work [31, 32]. Confidence in any such estimate is poor, since the absolute energy of the IF(D') state is unknown. However, if T_e for IF($A^3\Pi(2)$) were about 14 000 cm^{-1}, not an unreasonable estimate, then reaction (J) would promote IF($A^3\Pi(2)$) to approximately $v' = 7$ in the IF(B) manifold.

If this were the case, reaction (J) would provide an entrance channel into the IF(B) state which would explain the anomalously hot vibrational distribution in the population distributions calculated from the spectra in Fig. 1. Thus reactions (A) - (C), (F) and (H) - (J) all describe a possible pumping mechanism. This mechanism cannot be considered further until the rate constant for reaction (F) is known. Betts *et al.* [33] have measured the rate constant for reaction (F), where $I(^2P_{1/2})$ atoms were generated by the $O_2(^1\Delta) + I_2$ reaction scheme, and found it to be $(2 \pm 1) \times 10^{-13}$ cm^3 s^{-1}. A laser photolysis atomic resonance absorption experiment is being performed currently by the author to measure this rate constant. This experiment has a much less complex chemical environment, where the kinetic analysis will be simpler and the potential for competing reactions is greatly reduced. Also this mechanism cannot be considered further before both the controversy concerning the branching ratio for reactions (A) and (B) and the absolute value of T_e of the IF(A$^3\Pi(2)$) state are resolved.

An alternative mechanism would proceed by sequential pumping by $O_2(^1\Delta)$ up the IF(X) vibrational manifold. If the exothermicity of the $F + I_2$ reaction should favor IF(X) $v'' > 0$ production [27, 34] as in reaction (B), the IF(B) excitation could be achieved by sequential pumping of two $O_2(^1\Delta)$ molecules, reactions (D) or (G) followed by (H), (I) or (J). There is some experimental evidence to support such a mechanism; as stated above, the intensity of the IF(B–X) luminescence was maximized by arranging that all reagents, I_2, F–F$_2$ and $O_2(^1\Delta)$, mix simultaneously. When, for example, the fluorine atoms and I_2 were mixed upstream of the $O_2(^1\Delta)$ inlet the emission intensity was greatly reduced [12]. Under such conditions the IF(X) $v'' > 0$ product could vibrationally relax to IF(X) $v'' \approx 0$ before reacting with $O_2(^1\Delta)$.

5. Conclusion

The molecular dynamics of the IF(B$^3\Pi(0^+)$) and IF(X$^1\Sigma^+$) states as examined in the studies of Clyne *et al.* and Davis *et al.* indicate that the IF(B–X) transitions should be ideal candidates on which to establish a chemically pumped laser. Initial evidence indicated that $O_2(^1\Delta)$ would be an attractive energy storage–transfer partner for such a device. However, photon yield measurements indicate a poor efficiency. Low photon yields can be explained in part by the need for sequential $O_2(^1\Delta)$ pumping and non-radiative loss of IF(B). The latter would be due to the possibility of pumping IF(B) beyond its predissociation limit both by collisional excitation from the A$^3\Pi(1)$ state and by collisional ladder climbing out of the bound region of the B$^3\Pi(0^+)$ manifold. Recent measurements of large IF(B) quenching rates by $O_2(^3\Sigma)$ and water [33, 35], essentially unavoidable in high yield $O_2(^1\Delta)$ generation, coupled with the above conclusions probably diminish the potential of this chemical laser system. However, the search continues for a more suitable energy storage transfer partner for IF pumping.

Acknowledgment

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