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Final Report

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Lasing Characteristics of Gas Mixtures Involving UF_6: Application to Nuclear Pumping of Lasers

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by

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INTRODUCTION:

Our research efforts during this past year of NASA sponsorship have concentrated on identifying atoms or molecules that are attractive as potential nuclear-pumped lasers. These studies have led to the examination of the iodine-monofluoride (IF^*) molecule. Specifically, as a direct result of NASA funding, the following accomplishments have been realized in the past year:

1) The blue-green emission spectrum of IF^* in e-beam excited Ar, NF_3 and CF_3I mixtures has been observed and assigned to the $E \rightarrow A^3\Pi_1$ transition.

2) From fluorescence measurements, the radiative lifetime of the excited molecule has been estimated to be $\sim$ 15 ns.

3) The IF^* kinetic formation chain has been determined to be: $Ar^* \rightarrow Ar_2^* \rightarrow I^* \rightarrow IF^*$, where * indicates an electronically excited state of the atom or molecule indicated

and

4) The rate constants for quenching of I^* and ICl^* by various atoms and molecules (including UF_6) have been measured.

Simply stated, IF appears to be a very attractive choice for a laser to be pumped by the gaseous core reactor. For instance, the $E \rightarrow A^3\Pi_1$ band of IF lies in the blue-green and, therefore, UF_6 ground state absorption will be negligible. Also, quenching of IF^* by UF_6 is sufficiently small that a potential IF laser would be compatible with $\sim$ 1-10 Torr of UF_6. Also, since IF contains one fluorine atom, then UF_6 can be used to form the laser's upper state.

Finally, the highly structured nature of the IF^* blue-green emission band, the short ($\sim$ 15 ns) IF^* radiative lifetime and the Franck-Condon shift between the IF E and $A^3\Pi_1$ states all indicate that the small signal optical gain from IF^* should be large.

In the last two months, a research group at Garching has succeeded in obtaining stimulated emission from IF. Lasing occurs at $\lambda = 491$ nm. It is our intention of continuing the study of IF^* and, in particular: 1) to measure the pump power threshold for the laser and 2) determine the efficiency of an IF^* oscillator or the extraction efficiency of a dye-laser saturated IF^* amplifier.

The experimental results obtained during this past year are presently being written up for publication. However, the highlights of this experimental effort are summarized in the attached paper which has been submitted for publication.

IODINE-MONOFLUORIDE (IF) EMISSION SPECTRUM AND FORMATION KINETICS IN ELECTRON BEAM PRODUCED PLASMAS*

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ABSTRACT

Intense blue-green fluorescence from a structured band centered at $\lambda \sim 484$ nm has been observed from Ar, CF_3I and NF_3 gas mixtures ($T = 300°K$) excited by a ∿ 3 ns FWHM electron beam. This emission is tentatively assigned to the $E \rightarrow A^3\pi_1$ transition of the iodine-monofluoride (IF) molecule. From the temporal behavior of the IF^* and I_2^* (342 nm) emission, it has been determined that the IF(E) level is formed primarily by excitation transfer from I^* (^4P) states. The fluorescence efficiency of the IF($E \rightarrow A$) band and the IF^* (E) state radiative lifetime have been estimated to be ∿ 6% (in 99.83% Ar/.13% CF_3I /.04% NF_3 mixtures, $P_{TOTAL} \overset{\sim}{\sim} 2300$ Torr) and ∿ 15 ns, respectively. The emission band structure, the short IF(E) radiative lifetime and the Franck-Condon shift between the E and A states suggest that IF^* is an attractive candidate for a blue-green laser.

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The spectroscopic properties of the diatomic halogen molecules have been studied extensively for several decades and since 1975, stimulated emission has been obtained from each member of this molecular family (I_2, Br_2, $C\ell_2$ and F_2).[1]

In contrast, although numerous studies of the low-lying $A^3\pi_1$ and $B^3\pi^+_0$ states of the interhalogen molecules (BrF, $IC\ell$, etc.) have been conducted,[2-5] for many of these molecules little detailed information regarding higher excited states is available. Consequently, only recently have the interhalogens received attention as UV and visible laser candidates.

Huestis and co-workers[6] have observed strong fluorescence bands (from electron beam (e-beam) excited Ar and $IC\ell$ or IBr gas mixtures) at 385 and 430 nm which were attributed to ionic to covalent transitions of IBr and $IC\ell$, respectively. Optical gain was observed on the blue $IC\ell$ band but, due to ground state $IC\ell$ absorption,[6,7] oscillation was not obtained. Diegelmann et al[8] subsequently reported lasing at 285 nm from the $C\ell F$ molecule when formed in e-beam excited $Ne/F_2/C\ell_2$ gas mixtures. However, the identity of the states responsible for these e-beam pumped $IC\ell$, IBr or $C\ell F$ emission bands remains unclear.

The observation of intense blue-green spontaneous emission from e-beam excited $Ar/CF_3I/NF_3$ gas mixtures is described here. To our knowledge, this emission band, which peaks near $\lambda \sim 484$ nm, has not been reported previously[9-11] and is tentatively assigned to the $E \rightarrow A^3\pi_1$ transition of the iodine-monofluoride (IF) molecule. Both CF_3I and CH_3I have been utilized as iodine donors to minimize absorption in the 450-500 nm spectral region.[12-14]

The experimental apparatus used in these studies consisted simply of a Febetron 706 e-beam generator, an optical cell and gas handling equipment and a detection system. After traversing a ∿ 1 cm thick atmospheric drift region, an intense (∿ 1 kA-cm^{-2}), ∿ 3 ns FWHM beam of 600 keV electrons irradiated a mixture of Ar, CF_3I and NF_3 contained in a stainless-steel cell. The emission from the excited gases was viewed transverse to the e-beam axis by a 0.6 m spectrograph (in first order) and Polaroid Type 57 (or Kodak Tri-X) film and by a biplanar photodiode with an S-20 surface. Bandpass or calibrated neutral density filters were placed in the optical path to prevent saturation of the photodiode and to isolate the desired spectral region. Research grade rare gases and technical grade CF_3I, NF_3 and F_2 (as supplied by the manufacturer) were used in these experiments. Passivation of the e-beam cell and gas handling system was accomplished by allowing ∿ 50 Torr of F_2 to stand in the cell for ∿ 0.5 h. Finally, calibration of the observed spectra was afforded by a Hg pen lamp.

Upon exciting 2000–4000 Torr Ar, 3 Torr CF_3I and 1 Torr NF_3 gas mixtures with the e-beam, the intense blue-green emission band shown in Fig. 1 was observed. Vibrational structure in the band is evident and maximum emission occurs for λ ∿ 484 nm but the fluorescence extends to wavelengths < 430 nm. When either the NF_3 or CF_3I was removed from the gas mixture, the band of Fig. 1 vanished. Also, the same spectrum was recorded (although with diminished intensity) if NF_3 was replaced by F_2 or if He or Ne was used as the mixture diluent. Therefore, this blue-green band is attributed to the diatomic iodine-monofluoride molecule (IF) and is the longest wavelength diatomic halogen emission yet observed for relativistic electron beam excitation. Table I shows that the ∿ 484 nm peak wavelength of the IF spectrum is consistent with the known wavelengths[3,6] of the other iodine-monohalide emission bands (e-beam produced).

In order to identify the electronic states responsible for the 484 nm emission, an analysis of the <u>ICℓ and IBr</u> spectra (from e-beam irradiated Ar, CF_3I and $Cℓ_2$ or IBr gas mixtures) was undertaken. This approach was adopted simply because the excited states of ICℓ and IBr are better known than those of IF. For ICℓ, a close coincidence was found to exist between the measured emission spectrum and $v' = 0,1 \rightarrow v'' = 3$-6 transitions of the ICℓ ($E \rightarrow A^3\pi_1$) band, as calculated from the spectroscopic constants and vibrational transition assignments given by Rosen.[3] The peak ICℓ emission at 433 nm was identified as the (0,4) transition of the $E \rightarrow A^3\pi_1$ band. A similar analysis of the e-beam excited IBr band led to an analogous conclusion: that the band peak at λ ∿ 356 nm corresponds to the (0,4) transition of the $D \rightarrow A^3\pi_1$ band.[15] Neither the ICℓ nor IBr spectra could be explained by assuming $B^3\pi_0^+$ to be the lower energy state,[8] a result which may bear on attempts to identify the origin of the 342 nm band of I_2.[16,17]

Preliminary analysis[18] of the wavelength separation between the local maxima of the IF* emission spectrum (Fig. 1) suggests that ω_e (upper level) ∿ 250 cm^{-1}. Hence if the emission band peak at λ ∿ 484 nm is assigned to the $E \rightarrow A$ (0,4) transition (consistent with the ICℓ and IBr spectra), then $T_e(E)$ ∿ 37967 cm^{-1}. Table I shows that these rough estimates of T_e and ω_e are in agreement with the trends established by I_2, IBr and ICℓ. Moreover, if ω_e and T_e of the E state are taken to be those estimated here, then the vibrational lines in the IF* spectrum apparently originate from the v' = 0,1 levels of the E state and terminate on v'' = 3-6 of the $A^3\pi_1$ level.

In addition to the IF band, the only emission detected (from the Ar/CF_3I/NF_3 plasmas) between 250 and 650 nm was due to I_2^* (342 nm). So, in order to investigate the formation kinetics of the IF* molecule, the temporal behavior of both the I_2^* and IF* fluorescence was recorded using bandpass filters (I_2^*:T_{max} = 18% at λ_0 = 352 nm, $\Delta\lambda$ = 12 nm FWHM; IF*:T_{max} = 70% at λ_0 = 495 nm, $\Delta\lambda$ = 38 nm FWHM). Over a wide range of gas mixture compositions, the time decay of IF* and I_2^* waveforms (for an example, see Fig. 2) was found to be identical to within experimental error. This suggests that these excited molecules are fed by a common precursor. A similar conclusion was reached in ref. 6 from experiments involving Ar/ICℓ plasmas. Partial energy level diagrams for Ar, I, I_2 and IF are illustrated in Fig. 3. The I_2 states were redrawn from refs. 16 and 19 and the IF (X and A) levels were taken from the paper by Birks, Gabelnick and Johnston.[11] The E state of IF is included simply to indicate its position relative to the I_2^* (1432, $^3\pi_{2g}$) state but its equilibrium radius is probably slightly larger than shown in the Figure. Clearly, at least one of the I* (^4P) levels has sufficient energy to simultaneously break either the CF_3-I or NF_2-F bonds (2.32 and 2.52 eV, respectively) and populate low vibrational levels of I_2^* or IF*. Consequently, the kinetic scheme for IF* production is expected to be analogous to that proposed by Huestis et al for ICℓ.[6] That is:

$$\mathrm{Ar}^* \ (\mathrm{or}\ \mathrm{Ar}^*_2) + \mathrm{CF_3I} \xrightarrow{k_1} \mathrm{I}^* \ (^4\mathrm{P}) + \mathrm{CF_3} \qquad (1)$$

and

$$\mathrm{I}^*(^4\mathrm{P}) + \begin{cases} + \mathrm{NF_3} \xrightarrow{k_2} \mathrm{IF}^* \ (\mathrm{E}) + \mathrm{NF_2} & (2) \\ + \mathrm{CF_3I} \xrightarrow{k_3} \mathrm{I_2}^* \ (1432,\ ^3\pi_{2g}) + \mathrm{CF_3}, & (3) \end{cases}$$

where Ar^* represents one of the low-lying Ar (^{3}P) states and $\mathrm{Ar_2}^*$ is the metastable $^3\Sigma_u^+$ excimer state.

Figure 4 shows the dependence of the time and wavelength integrated IF^* fluorescence on the argon partial pressure for Ar, 2 Torr $\mathrm{CF_3I}$ and 1 Torr $\mathrm{NF_3}$ gas mixtures. Initially, the integrated spontaneous emission increases as $\sim [\mathrm{Ar}]^2$, which suggests that $\mathrm{Ar_2}^*$ may be primarily responsible for I^* formation in Eqn. (1). Above ∿ 2300 Torr, the IF^* fluorescence levels off due to increased Ar quenching of the molecule. Here, it should be noted that the internal energy of the Ar_2^* ($^3\Sigma$) molecule is $\lesssim 1000\ \mathrm{cm}^{-1}$ in excess of that required to break the $\mathrm{CF_3}$-I bond and subsequently excite I to the $6s^4P_{1/2}$ or 3/2 levels. However, Ar^* (^{3}P) atoms are capable of populating I^* states $\sim 3 \cdot 10^4\ \mathrm{cm}^{-1}$ above the ^{4}P levels. Also, the $\mathrm{Ar_2}^*$ excimer formation process, $\mathrm{Ar}^*\ (^3\mathrm{P}) + 2\ \mathrm{Ar} \rightarrow \mathrm{Ar_2}^*\ (^3\Sigma) + \mathrm{Ar}$, competes with Eqn. (1) for the available Ar^* (^{3}P) atoms. Taking the $\mathrm{Ar_2}^*$ formation rate[20] to be $1.7 \cdot 10^{-32}\ \mathrm{cm^6\text{-}s^{-1}} \cdot [\mathrm{Ar}]^2$ and letting $k_1 = 4.7 \cdot 10^{-10}\ \mathrm{cm^3\text{-}s^{-1}}$[21] then for 3 Torr $\mathrm{CF_3I}$ and $p_{Ar} > 1700$ Torr, $\mathrm{Ar_2}^*$ formation is the dominant Ar^* (^{3}P) loss mechanism. The apparent conclusion, then, is that for the high Ar pressure gas mixtures characteristic of these experiments, the $\mathrm{Ar_2}^*$ molecule, rather than an Ar^* (^{3}P) atom, is the immediate precursor to the I^* (^4P) state.

From the single exponential decay of the IF^* waveforms from low pressure ($P_{TOTAL} \lesssim 10$ Torr) CF_3I/NF_3 gas mixtures, the IF^* (E) state radiative lifetime has been estimated to be $\approx$ 15 ns.[22] This result is consistent with the $\sim$ 7 ns lifetime for the upper state of the I_2^* 342 nm band.[19,23] Therefore, the waveforms shown in Fig. 3 (for Ar, CF_3I and NF_3 mixtures) reflect the quenching of I^* by CF_3I or NF_3. Measurements of the rate constants for collisional quenching of I^* by various atoms and molecules and the IF^* radiative lifetime will be described elsewhere.[22]

Finally, by comparing the time-integrated IF^* blue-green fluorescence to the N_2 ($C \rightarrow B$) emision from Ar/5% N_2 gas mixtures,[19] the fluorescence efficiency of the IF^* ($E \rightarrow A^3\pi_1$) band in e-beam produced 2300 Torr Ar/3 Torr CF_3I/1 Torr NF_3 mixtures was found to be $\sim$ 6%. Also, measurements of the branching ratio for IF^* formation by quenching of I^* ($BR \equiv \int IF^*(\lambda,t)d\lambda dt / \int (IF^* + I_2^*)d\lambda dt$) in 2300 Torr Ar, p_{CF_3I}, 1 Torr NF_3 gas mixtures revealed that $25\% \leq BR \leq 44\%$ for $4 \geq p_{CF_3I} \geq 1$ Torr.

In summary, strong blue-green fluorescence has been observed from electron beam excited Ar, CF_3I and NF_3 gas mixtures. This emission has been tentatively assigned to the $E \rightarrow A^3\pi_1$ transition of the IF molecule and is likely the same transition that is responsible for the 385 and 430 nm bands of IBr and ICℓ, respectively. The emission spectrum and short radiative lifetime of IF^* and the Franck-Condon shift between the E and A states make the molecule attractive as a potential laser. Also, none of the ground or excited state species that are known to be present in $Ar/CF_3I/NF_3$ plasmas absorb strongly in the 480-500 nm spectral region. Since it would likely operate at room temperature, an IF blue-green oscillator would represent an improvement over the HgBr laser which requires operating temperatures in excess of 100°C. Consequently, experiments to obtain lasing from this molecule using both e-beam and discharge pumping are in progress.

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TABLE I

Peak emission wavelengths and spectroscopic constants for the e-beam excited iodine-monohalide bands.

MOLECULE	λ_{PEAK} (nm)	UPPER ENERGY LEVEL		
		DESIGNATION	ω_e (cm^{-1})	T_e (cm^{-1})
I_2	342	$E(1432, {}^3\pi_{2g})^{(a)}$	104.2	~ 40,000
IBr	386	$D^{(b)}$	90.1	38,713
ICℓ	433	$E^{(b)}$	174.2	37,741
IF	484	E	~ $250^{(c)}$	~ $37,967^{(c)}$

(a) The identity and spectroscopic constants of the upper level of the I_2 342 nm band are still somewhat uncertain; see refs. 16 and 17.

(b) Ref. 3.

(c) Estimated, this work.

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FIGURE CAPTIONS

Fig. 1. Densitometer tracing of the IF^* emission spectrum observed from e-beam excited 99.83% Ar, 0.13% CF_3I, 0.04% NF_3 ($p_{TOTAL} = 2300$ Torr) gas mixtures. The spectrograph resolution was 0.16 nm and the vertical scale is linear in optical density. The same spectral profile was observed regardless of the iodine/fluorine donor molecules or rare gas diluent used in the mixture.

Fig. 2. Temporal decay of the I_2^* (342 nm) and IF^* (484 nm) fluorescence waveforms for a 2300 Torr Ar/3 Torr CF_3I/1 Torr NF_3 gas mixture. The I_2^* and IF^* emissions were spectrally isolated by bandpass filters. For clarity, the IF^* waveform has been intentionally displaced horizontally with respect to the I_2^* trace.

Fig. 3. Partial energy level diagrams for the atomic and molecular species involved in IF^* formation in e-beam produced plasmas. The I_2 and IF (X and A) energy levels were redrawn from refs. 16 and 19 and ref. 11, respectively. Only the I^* ($^4P_{1/2}$ and $^4P_{5/2}$) states are shown for clarity. At the bottom of the graph are also shown the NF_2-F and CF_3-I bond energies.

Fig. 4. Variation of the time and wavelength integrated IF^* fluorescence with the Ar partial pressure for p_{Ar}/3 Torr CF_3I/1 Torr NF_3 gas mixtures.

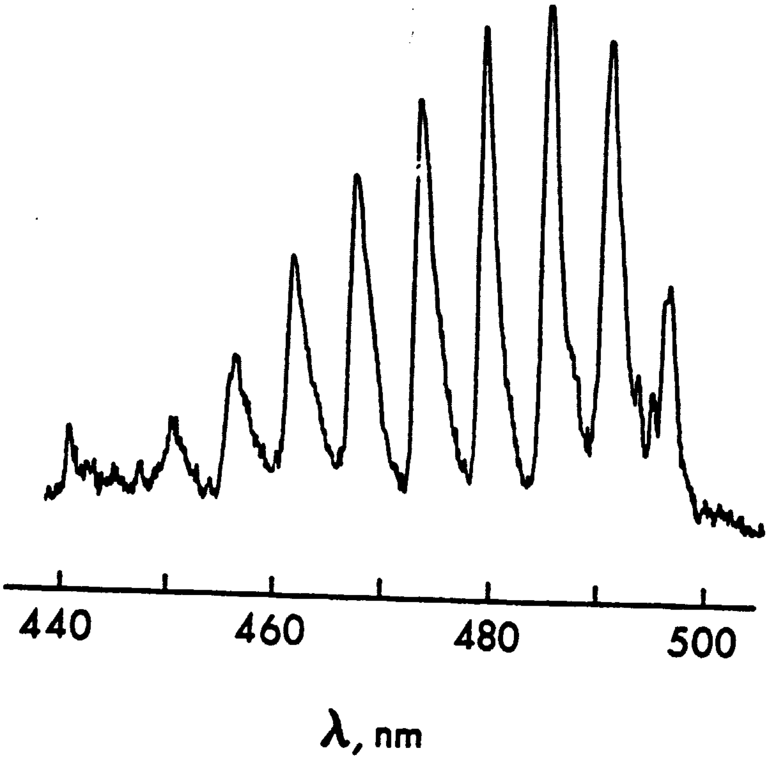

Fig. 1 Hutchison et al.

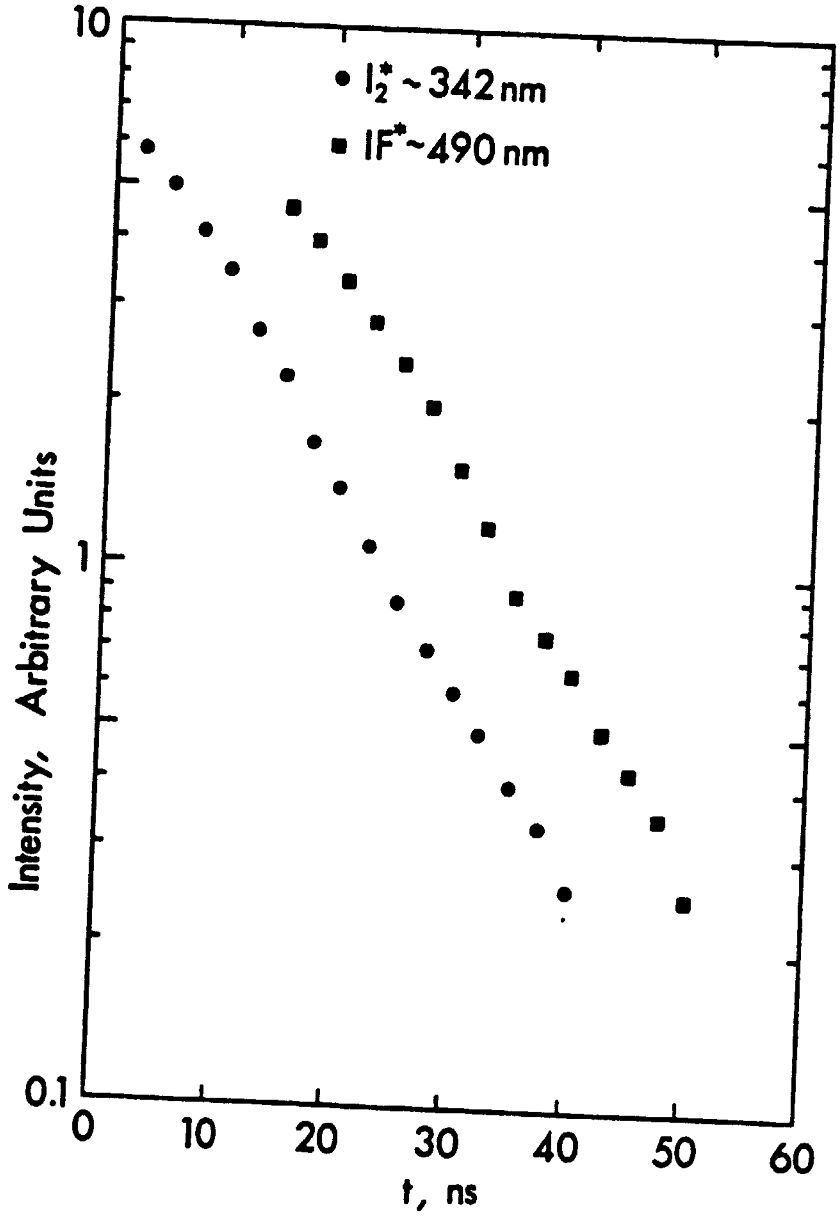

Fig. 2 Hutchison et al.

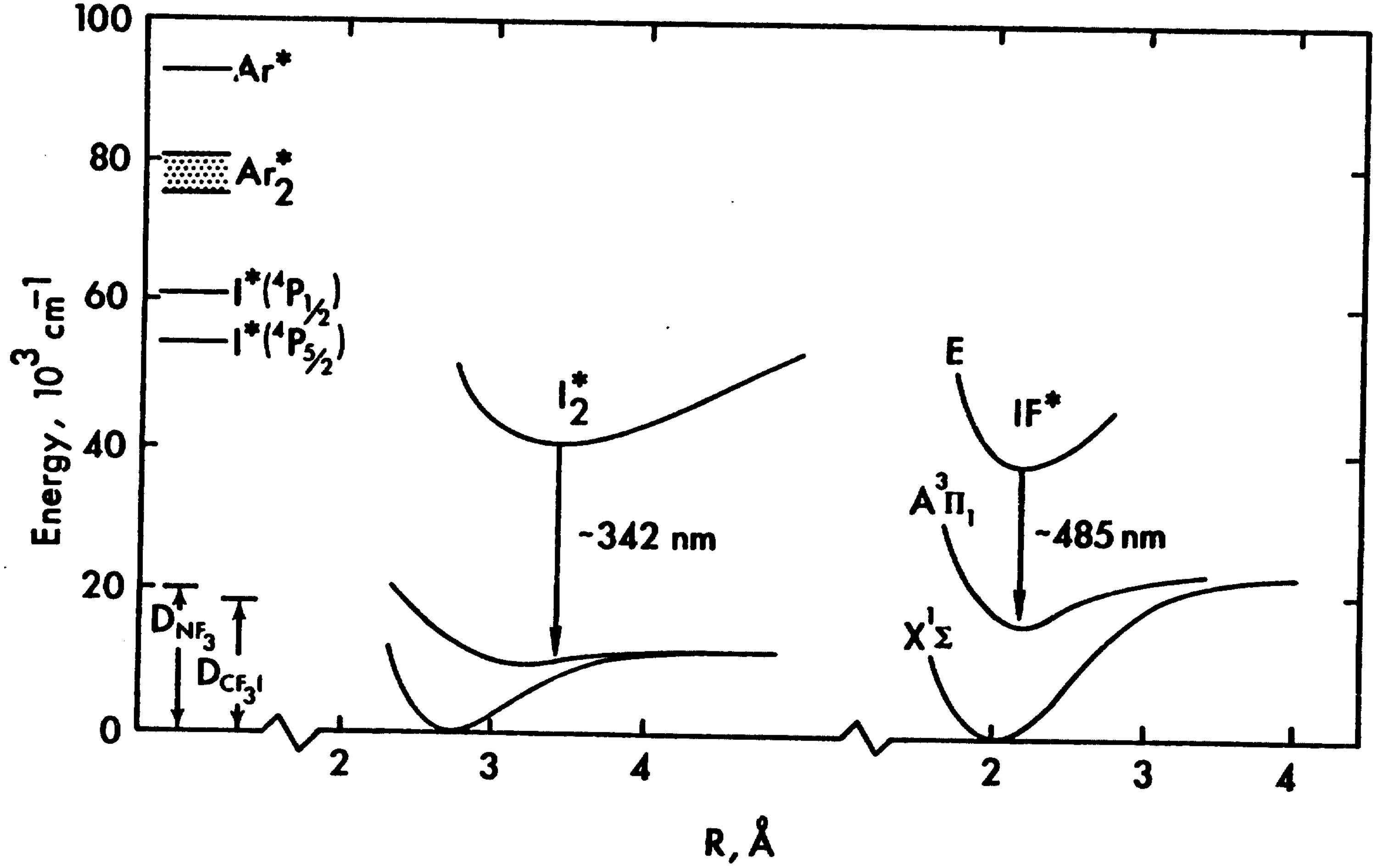

Fig. 3 Hutchison et al.

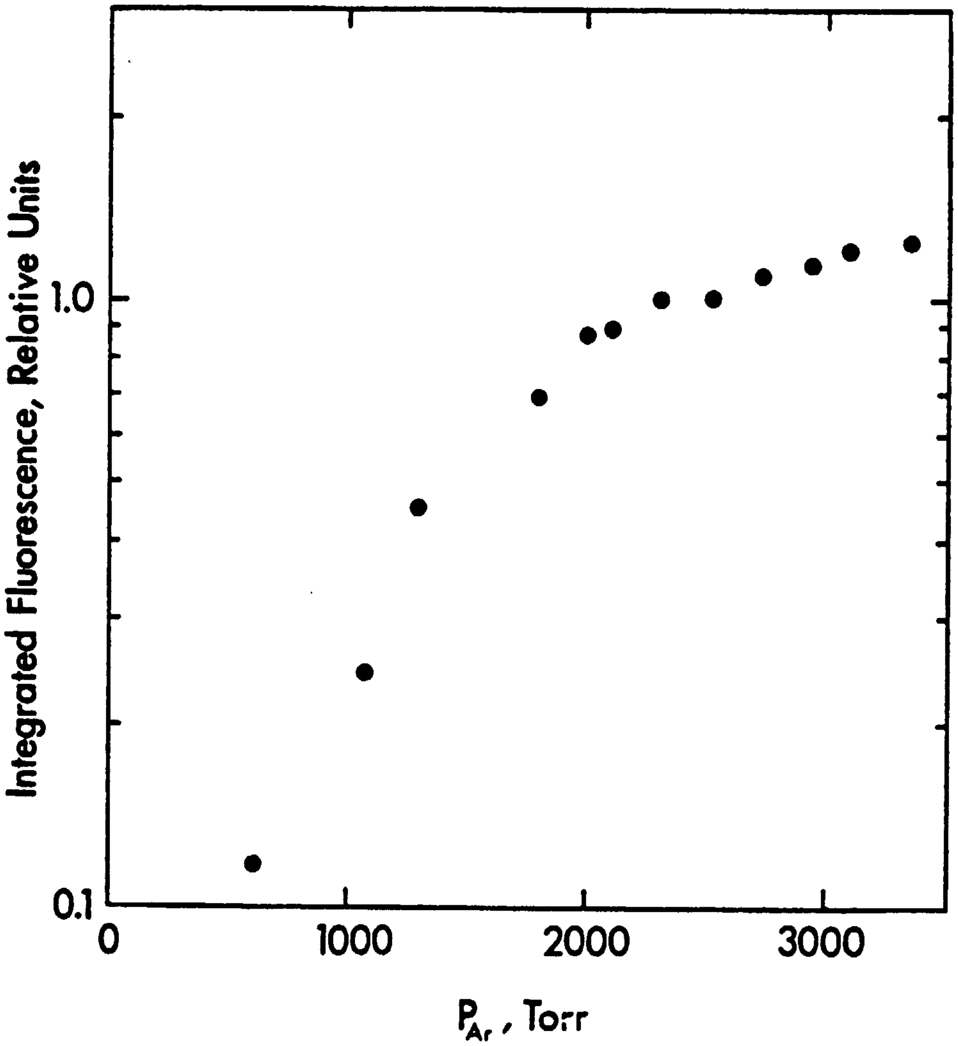

Fig. 4 Hutchison et al.