Emission Spectra of IF from a Corona-Excited Supersonic Jet Discharge[†]

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High-resolution emission spectra of IF from a corona-excited supersonic jet discharge are presented. Six vibrational bands of the D′2–A′2 transition were rotationally analyzed for the first time, as well as four bands of the EO⁺–XO⁺ transition. A study of the Ω-type doubling observed for the high-J rotational levels of D′ has provided estimates for the relative energy differences between the electronic origins of the first-tier ion-pair states.

Introduction

Iodine monofluoride, IF, is one of the most challenging diatomic halogens to study. Although the molecule is stable in the gas phase, it quickly disproportionates to I_2 and IF_5 in a static cell.[1] Consequently, IF is usually made in an electrical discharge or flow reactor.

Precise information on the ion-pair states of IF is extremely sparse. The first-tier ion-pair states of IF dissociate to $I^+(^3P_2)$ + $F^-(^1S_0)$, and the three resultant molecular potential energy curves which arise from this combination of ionic terms are labeled in Hund's case (c) nomenclature: EO⁺, $\beta1$, and D′2. To date, rotational constants for β are unknown and only preliminary results for D′ are available.[2] Clark and Littlewood (CL) determined rotational constants and term values for 11 vibrational levels of EO⁺ by using a (1 + 1) multiphoton excitation scheme.[3] Many of the parameters that characterize the E-state potential energy curve should also apply approximately to β and D′, since the dominant interaction that binds the molecule in an ion-pair state is Coulombic. Each state is expected to have a dissociation energy of $\approx$38 800 cm^{-1}, a vibrational frequency of $\approx$250 cm^{-1}, and an equilibrium bond length of $\approx$2.8 Å.[4]

There is a considerable interest in the D′2 state in particular, since it is the upper level of the well-known IF laser transition near 490 nm.[5-12] The lower lasing level is the relatively unknown A′³Π(2) valence state, whose electronic origin is expected to lie in the infrared region with respect to the ground state $X^1\Sigma^+(O^+)$. Interest in efficient blue-green lasers has been growing, motivated in part by applications in ocean optics[13] and photochemistry.[14] The D′–A′ transition of IF is an attractive candidate in this regard, since it can be tuned between 479 and 498 nm, with a maximum output near 490.7 nm. The main obstacle for multiphoton entry into D′ using lasers is a strong $\Delta\Omega = 0$ "propensity" rule governing valence to ion-pair transitions. This forces the initial step of a multiphoton process to be a two-photon transition to A′, using typically unavailable far-infrared wavelengths.

Recently, we demonstrated that emission spectra of the D′–A′ transition of I_2[15] and IBr[16] could be readily photographed from a corona-excited supersonic expansion (CESE). In this work, like techniques were successfully used to record emission spectra of the D′–A′ transition of IF, from which rotational constants for both electronic states are reported for the first time.

Experimental Section

A CESE source provides a near-ideal medium for studying IF, since it combines an electrical discharge with a flow system.[15,16] Two reaction routes were successful in producing IF. Initially, the molecule was made by discharging iodotrifluoromethane, CF_3I (Aldrich), in argon, Ar (Canadian Oxygen Limited, commercial grade). Since CF_3I was only available in small allotments, IF was produced in subsequent experiments by discharging a mixture of iodine, I_2 (BDH, reagent grade), and tetrafluoromethane, CF_4

(Freon-14, Matheson), diluted in Ar. For the latter route, I_2 was maintained at first in a heated glass bulb external to the chamber. The resultant vapor was entrained in the CF_4/Ar carrier gas and delivered to a Pyrex nozzle mounted into the vacuum chamber. Since the I_2 vapor tended to condense inside the gas lines and vacuum connectors, a different nozzle configuration, shown in Figure 1, was developed which eliminated many of these problems.

The relatively nonvolatile I_2 crystals were inserted inside the "bulb" nozzle through a side arm just above the pinhole. The side arm was sealed with a Teflon plug. Nichrome wire was wrapped around the bulb and held in place with asbestos tape. The bulb was mildly heated under vacuum by connecting the ends of the nichrome wire to an external dc power supply (Hewlett-Packard 6286A) via a hermetically sealed BNC connector located on one of the chamber flanges.

The nozzle, having an $\approx$500-μm-diameter pinhole, was sealed into an X-Y-Z translator mounted on the vacuum chamber, which was evacuated to <50 mTorr by a mechanical pump (Edwards E2M80) and Roots blower (Edwards EH1200) combination. Continuous free supersonic jets were produced at a stagnation pressure of $\approx$20 psia.

A corona discharge was excited by applying positive voltage to a stainless steel electrode running down the central axis of the nozzle. The chamber itself served as the grounded cathode. Typical operating conditions were $\approx$800 V and 40 mA. Heating conditions and reactant gas partial pressures were determined by trial and error for each experiment by visually monitoring the jet until a blue-green emission was observed, indicating the presence of IF. Emission from the jet was imaged onto the entrance slit (40 μm) of a 3.4-m air spectrograph (Jarrel-Ash 70-000) and photographed in 11th order with a reciprocal dispersion of $\approx$0.46 Å/mm. Order separation was achieved by using either band-pass filters ($\Delta\lambda \approx$ 75 nm, Optikon Corp.) or a Pellin-Broca prism predisperser.

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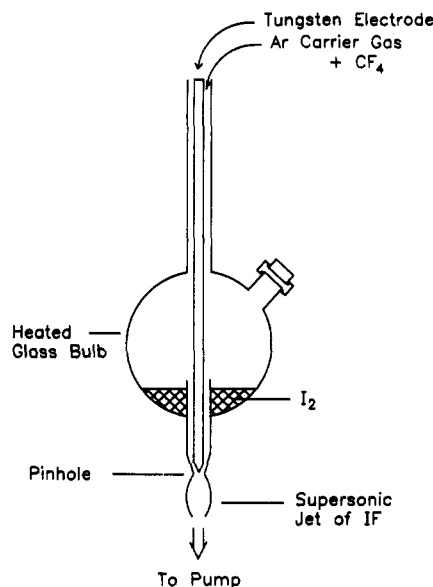**Figure 1.** A schematic of the "bulb" nozzle used to produce IF from a corona-excited supersonic expansion.

Figure 2. A schematic of the IF potential energy curves of interest in this work. The assignments of the 490- and 410-nm band systems are indicated by vertical arrows.

Typical exposure times ranged between 20 min and 2 h for Kodak Tri-X Pan film. Spectra for the weaker IF features were also recorded on Kodak TMAX P3200 high-speed film. Exposures times for this film were reduced by a factor of ≈4 compared with Tri-X, but the grain was coarser.

Calibration was provided by Fe and Ne hollow cathode lines in overlapping orders. Films were measured on a Nikon profile projector, Model 6C.

Observed Spectra and Assignments

When CF_3I or $CF_4 + I_2$ was discharged in Ar, the strongest spectral features were due to the well-known $d^3\Pi_g-a^3\Pi_u$ (Swan bands) and $C^1\Pi_g-A^1\Pi_u$ (Deslandres–d'Azambuja bands) transitions of diatomic carbon, C_2.[17] The remaining bands were assigned to transitions of IF.

Two electronic systems of IF were found near ≈490 and ≈410 nm. Due to the aforementioned "propensity" rule for parallel ion-pair to valence transitions, four band systems might be expected in this general region: $D'2-A'2$, $\beta1-A1$, $E0^+-B0^+$, and $E0^+-X0^+$ (Figure 2). The 490-nm bands were observed previously from electron beam pumping experiments and were assigned to $D'-A'$.[5,6] The weaker system at 410 nm was noted by Diegelemann et al. but not explained.[6] Since the electronic origins of the first-tier ionic states of interhalogens are usually nearly coincident, E–B is expected to lie to the red of $D'-A'$.[4] The β–A system should resemble $D'-A'$ with a local lower state $\Delta G_{v+1/2}$ roughly equal to that for $D'-A'$ (≈250 cm^{-1}). The observed ΔG of the 410-nm system (≈370 cm^{-1}) was inconsistent with this expectation. Therefore, the 410-nm system was assigned to E–X.

Six vibrational bands of $D'-A'$ and four vibrational bands of E–X were rotationally analyzed. Since the E state of IF had previously been characterized by CL,[3] analysis of the rotational structure of the E–X transitions near 410 nm was routine. The four bands were assigned to transitions originating from $v_E = 0$. Line frequencies were fitted to a Dunham expansion to obtain molecular constants.

The overall intensity distribution of the $D'-A'$ band system evident in our spectra, as well as in lower resolution studies,[5,6] strongly suggested that the four most intense transitions analyzed in this work formed a lower state progression originating from $v_{D'} = 0$. One of these bands is shown in Figure 3. Two weaker hot bands from $v_{D'} = 1$ forming a sequence progression were also analyzed. Since transitions with $v_{D'} > 1$ were not observed, we
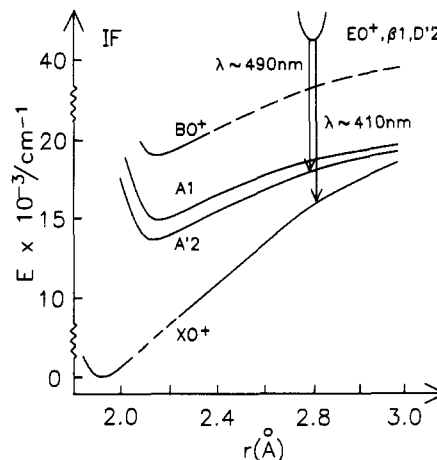
conclude that the jet was characterized by a relatively low vibrational temperature. The remaining bands observed in low resolution could not be measured in this work due to severe overlapping with C_2 emission.

Since there is only one naturally occurring isotopomer of iodine monofluoride, $^{127}I^{19}F$, lower state vibrational numbering could not be determined from isotope shifts but depended instead on less reliable methods. Therefore, possible vibrational assignments will be presented following an outline of the procedure used to analyze the rotational structure of the observed bands.

Rotational Analysis

As expected for the $\Omega' = 2$ to $\Omega'' = 2$ transition shown in Figure 3, the P and R branches are strong while the Q branches are vanishingly weak.[18] Since each vibrational band is red-shaded, the band head is formed in the R branch. Each P(J) line is expected to lie near an R(J+δ) line, where δ is a positive integer. It was relatively straightforward to establish the absolute J numbering and the value of δ for each band since B_0 for D' was expected to be very close to that determined by CL for E.[3] Indeed, with that constraint, there proved to be only one δ and one absolute J numbering for each band which could predict the experimentally observed band head frequencies. The value of δ was 4 for the highest frequency band (lowest A' vibrational level observed), changing to 5 for the lower frequency bands (highest A' vibrational levels observed).

At high J (≥35), each rotational line was split into e and f parity components due to Ω-type doubling. The splittings were found to increase approximately as J^4 and were essentially the same for each band where high-J lines could be measured. The J^4 dependence confirmed the assignment of the 490-nm band system to a 2–2 transition.[18] Since the e/f splittings were the same for bands with a common upper vibrational level, they must arise in the D' state alone.

While it was possible to obtain effective constants from rotational lines where the Ω-type doubling was unresolved ($J \leq 35$) by using a simple Dunham expansion, the coefficient of the term in $J^2(J + 1)^2$ was found to be positive, which indicates a perturbation. Since D' is isolated energetically from the valence states or higher tier ion-pair levels, the perturbation must arise from interactions within the first tier. The first-tier states can only interact by rotational–electronic Coriolis coupling, since each is characterized by a different component of total angular momentum along the bond axis, Ω. The matrix element for this heterogeneous interaction is well-known and will only be summarized here.[19,20]

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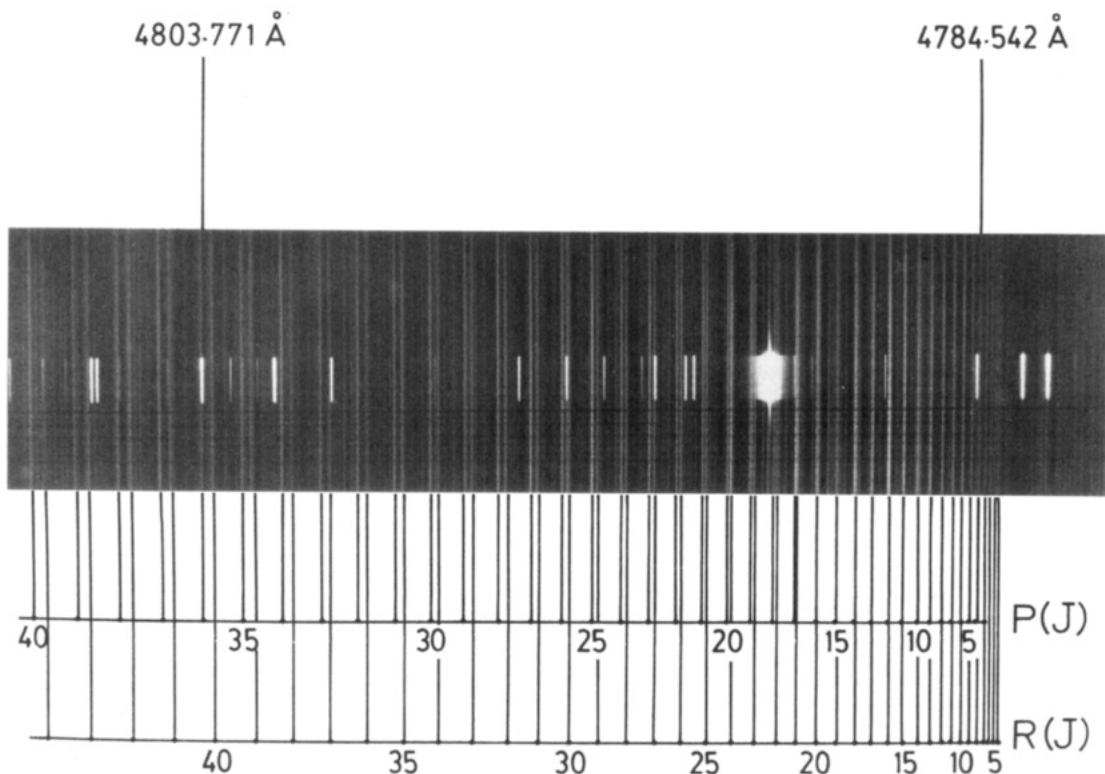(20) Hougen, J. T. *NBS Monogr.* (*U.S.*) **1970**, *No. 115*.

4803·771 Å   4784·542 Å

Figure 3. One vibrational band of the D′–A′ transition of IF near 480 nm which has been tentatively assigned to (0,20). At high J (>35) each rotational line is split due to Ω-type doubling.

Both e and f parity components of D′ and β are coupled by a matrix element of the form

$$H_{\Omega,\Omega'} = W_{\Omega,\Omega'} B_{v,v'}^{\Omega,\Omega'} [J(J + 1) - \Omega\Omega']^{1/2} \qquad (1)$$

where $B_{v,v'}^{\Omega,\Omega'}$ is given by

$$B_{v,v'}^{\Omega,\Omega'} = \langle \Omega, v | h/8\pi c\mu r^2 | \Omega', v' \rangle \qquad (2)$$

and is the off-diagonal rotational constant evaluated between vibrational wave functions v and v' of the two electronic states Ω and Ω', respectively. $W_{\Omega,\Omega'}$ is an electronic factor.

Pure precession is expected to hold for IF in agreement with all other halogens.[4] This assumes that the total angular momentum of the I^+ term, J_a (=$L + S$), is a good quantum number and is preserved in the IF molecule. In that case, $W_{\Omega,\Omega'}$ can be calculated from

$$W_{\Omega,\Omega'} = [J_a(J_a + 1) - \Omega\Omega']^{1/2} \qquad (3)$$

where $J_a = 2$ for the first tier.

The e levels of β are coupled to the levels of E (all e) by a similar matrix element which is multiplied by a factor of $2^{1/2}$.

The term $B_{v,v'}^{\Omega,\Omega'}$ was taken to be diagonal in v since the differences in bond lengths for the first-tier states were expected to be small. Thus, the rotational energy levels could be calculated by diagonalizing a 2 × 2 matrix for the f sublevels and a 3 × 3 matrix for the e sublevels.

A global fit was made of rotational transitions between $v = 0$ (up to $J \approx 65$) and $v = 1$ (up to $J \approx 35$) of D′ and four vibrational levels of A′, plus transitions between $v = 0$ of E (up to $J \approx 35$) and four vibrational levels of X. The lower states could be fitted either to Dunham expansions or, equivalently, to band origins and band-specific rotational constants. The upper levels were fitted by including the off-diagonal matrix elements described above and diagonalizing the resulting matrix. The on-diagonal matrix elements were taken to be the appropriate Dunham series in powers of $(v + \frac{1}{2})$ and $J(J + 1)$.

The main difficulty with this calculation lay in the numerical evaluation of the factors $B_{v,v'}^{\Omega,\Omega'}$ which required potential curves for the perturbing states.

A Morse potential for each ion-pair state was constructed from estimates for the equilibrium bond lengths, r_e, the vibrational

frequency, ω_e, and the first anharmonicity constant, $\omega_e x_e$, for each state. The value of $\omega_e x_e$ for D′ and β was fixed to the E-state result of 0.5 cm⁻¹.[3] The vibrational frequency for E was known,[3] while $\omega_e(D')$ was determined from band origins of the transitions measured in this work. The frequency for β was initially fixed at the E-state value of ≈ 250 cm⁻¹ but was later floated.

The r_e's were initially unknown, so an iterative process was adopted to determine them. An input set of r_e's was estimated, Morse potentials constructed, and $B_{v,v'}^{\Omega,\Omega'}$'s calculated by using the Numerov–Cooley method. These factors were then included in a nonlinear fit to determine an output set of Dunham parameters. The average of the input and output r_e's were used as input for the next cycle of refinement. The iterative process was continued until a self-consistent set of parameters was obtained.

Additional constraints were required for the global fit. The Y_{11} ($\approx -\alpha_e$) constants for E and β were calculated from the Pekeris formula assuming the values of Y_{10} ($\approx \omega_e$) and Y_{20} ($\approx -\omega_e x_e$) discussed above.[10] The centrifugal distortion constants Y_{02} ($\approx -D_e$) for D′, E, and β were constrained to $-4B_e^3/\omega_e^2$ while Y_{02} and Y_{03} ($\approx H_e$) for A′ were determined from RKR–Morse calculations described below. The final set of constants for the ion-pair states is presented in Table I, while those for the valence states are listed in Table II. Line frequencies and assignments for the 584 transitions used in the global fit are available as supplementary material.[21]

Initially, the relative energies of D′, β, and E were unknown. The parameters in Table I correspond to the electronic origin of D′ lying below β since the alternate scheme predicts avoided crossings between D′ and β, which would be evident in our spectra but were not observed. There remain two possible solutions to the calculation, the first with E above β and the second with E below. The former corresponds to the f levels lying higher than the e levels in D′ while the latter corresponds to the opposite scenario. The latter case is presented in Table I and is preferred because of a better overall fit ($\sigma = 0.028$ cm⁻¹ versus 0.035 cm⁻¹), especially for the higher J e/f splittings, and because for this solution only, the rotational B value determined for β was found

(21) See Supplementary Material Available paragraph at the end of the article.

TABLE I: Spectroscopic Parameters (cm⁻¹) for the First-Tier Ion-Pair States of IF

parameter[a]	E0⁺	β1	D'2
Y_{10}	248.6[c]	250.06 (42)	265.102 (17)
Y_{01}	0.133570 (81)	0.13052 (53)	0.122815 (41)
$10^4 Y_{11}$	-3.4[c]	-3.4[c]	-7.71 (37)
$10^7 Y_{02}$	-1.46[c]	-1.20[c]	-1.05[c]
Δ^b		103.9 (3.5)	26.90
$B_{0,0}^{1,\Omega}$		0.1278	0.0996
$B_{1,1}^{1,\Omega}$		0.1198	0.0527
$r_e{}^d$	2.76371 (84)	2.7958 (57)	2.76371 (48)

[a] 1σ standard deviation in brackets. [b] $\Delta = T_e(\beta) - T_e(\Omega)$. CL give $T_e(E) = 41\,291.96$ cm⁻¹.[3] [c] Constrained. [d] In angstrom units.

TABLE II: Band Origins, ν_0, and Lower State Rotational Constants (in cm⁻¹) for IF Transitions Observed from a CESE Source

$V_{D'}$	$V_A{}^a$	ν_0	B''
0	20	20 903.097 (7)[c]	0.180008 (21)
0	21	20 647.820 (7)	0.176460 (21)
0	22	20 403.264 (6)	0.172771 (23)
0	23	20 170.298 (8)	
1	23	20 435.400 (16)	0.168849 (24)
1	24	20 214.317 (17)	0.164604 (40)
V_E	$V_X{}^b$		
0	33	24 572.582 (7)	0.212146 (65)
0	34	24 190.908 (7)	0.209585 (67)
0	35	23 817.783 (7)	0.206943 (68)
0	36	23 453.103 (7)	0.204221 (69)

[a] For D'-A' $Y''_{02} = -5.23 \times 10^{-7}$ cm⁻¹ and $Y''_{03} = -3.2 \times 10^{-12}$ cm⁻¹. [b] For E-X $Y''_{02} = -2.91$ (21) $\times 10^{-7}$ cm⁻¹. [c] 1σ standard deviation in brackets.

to be intermediate between those for E and D', in agreement with all other known interhalogens.[4]

Vibrational Assignments

As indicated above, vibrational assignments are difficult to establish for IF, since there is only one naturally occurring isotopomer. CL believed they had excited E0⁺ ($v = 0$) in a multiphoton experiment since they were unable to observe transitions at lower energies.[3] While they recognized that this was not a proof for their vibrational numbering, their conclusions are accepted here, since they allow vibrational assignments for the transitions analyzed in this work to be determined.

By combining CL's E-state term values[2] with the E-X measurements of this study, absolute energies for our unknown X-state vibrational levels were determined. Precise ground-state molecular constants valid up to $v = 19$ have recently been reported.[21] Vibrational origins and rotational parameters for $v_x = 0$–19 were calculated from these results and then refitted along with the constants obtained from our transitions. The vibrational numbering of the present bands was varied while keeping the assignments of the known bands fixed, until a best fit was achieved. There was a clear preference for $v_x = 33$–36.

Although the extrapolation from $v_x = 19$–33 is large (>6000 cm⁻¹), the X state appears to be well-behaved. Therefore, our numbering is probably correct. An RKR potential valid over the entire range of observed vibrational levels was constructed to determine centrifugal distortion constants. These parameters were reasonably close those obtained from our least-squares fit. Calculated Franck–Condon factors were also consistent with the intensities of the observed E–X transitions, although they were not strongly dependent on the vibrational numbering of X.

The vibrational assignments for D'–A' are more problematic. Observed A' vibrational term values were calculated by using the rotational deperturbation calculation reported here and the E-state term values of CL.[3] Little is known about the A' state except from matrix-isolation studies.[23] In those experiments matrix

effects were found to relax gas-phase single-photon selection rules, allowing the normally forbidden transitions between X and A' to be observed. In this way, the electronic origin T_e of A' was estimated to be $\approx 13\,236$ cm⁻¹. By analogy with other halogens, the vibrational frequency and equilibrium bond length of A' should be close to those for the B state.[24] Consequently, the following procedure was adopted. The A' term values were fitted to a low-power Dunham expansion with the vibrational frequency (Y_{10}) fixed at the B-state value of ≈ 411 cm⁻¹.[22] Various vibrational numberings were tried, and the resultant T_e's were compared with the matrix-isolation result. The best agreement was obtained when the lowest observed A' level in this work was assigned to $v = 19$ or 20, with 20 being somewhat better. This represents an increase of 7 over the v_A' numbering scheme proposed by Diegelmann et al.[6] While it is difficult to assess the reliability of our assignment, it was found that the agreement between the higher order vibrational constants from the least-squares analysis, particularly Y_{20}, and those for the B state was best for this numbering.

As an internal check of the consistency of the vibrational analysis, Morse/RKR curves were constructed for the A' state. Here the width of the potential was derived from vibrational Dunham parameters using RKR f integrals, while the inner turning points were calculated from a Morse potential based on ω_e, $\omega_e x_e$, and r_e.[25] Using the r_e of the B state produced calculated rotational constants in very good agreement with observed values. Calculated Franck–Condon factors for the D'–A' transition were also in good agreement with the observed spectrum, but, as in the case for E–X, they were largely insensitive to the vibrational numbering of the A' state. The D'–A' transitions analyzed in this work are assigned to (0,20), (0,21), (0,22), (0,23), (1,23), and (1,24). If we use our numbering, the strongest lasing arises in the (0,22) band. The lower state vibrational numbering proposed here is probably good to ±1.

Discussion and Conclusions

Rotational constants for the D' ion-pair state and the A' valence state are reported here which are essentially in agreement with those determined by Salter[2] but are substantially more precise. An analysis of the Ω-type doubling has led to estimates of the relative energies, Δ, between D' and the other two ion-pair states in the first tier. While the high-J levels observed in this work were helpful for the rotational analysis, they also indicate that the supersonic jet was ineffective in cooling the IF sample. The stagnation pressure and current/voltage characteristics of the CESE need to be examined in a systematic way to determine the best conditions for reducing vibronic congestion. The standard errors listed in Table I, associated with the separations between ion-pair states are quite good, but do not reflect the inherent error due to the model used for the deperturbation calculation. For example, there was a strong correlation between the value of Y_{03} for the A' state and many of the important parameters in Table I. Changing Y_{03} by $\approx 30\%$ changed $\Delta_{\beta,D'}$ by ≈ 1 cm⁻¹, $\Delta_{\beta,E}$ by ≈ 10 cm⁻¹, and $B_{D'}$, B_β, and B_E by approximately twice their corresponding standard error, σ. These unusual results reflect the nature of our experimental evidence for the relative positions of D' and E. The e/f splittings in the D' state are related via the

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unseen β state to the position of the E state and provides the only clues to this quantity. Unfortunately, these splittings occur only at high rotational quantum numbers, and their calculation is thus affected by the nature of our model for centrifugal distortion. In view of the uncertainties associated with the A$'$ potential, including vibrational numbering, it seems more appropriate at this time to accept these large model-dependent effects than to use a more sophisticated model for centrifugal distortion.

The calculations were done assuming 100% pure precession. This approach was successful for ICl[19] and IBr[26] but less so for BrCl.[27] Assuming 95% of the pure precession value of $W_{\Omega,\Omega'}$ lowered $\Delta_{\beta,D'}$ by ≈ 1 cm^{-1}, $\Delta_{\beta,E}$ by ≈ 10 cm^{-1}, and $B_{D'}$, B_β, and B_E by roughly 1σ. Probably, 95% pure precession represents a reasonable lower limit for IF.

Based on the above, the following values for the principal parameters are suggested as being more reasonable:

$$\Delta_{\beta,D'} = 26.9 \ (1) \qquad \Delta_{\beta,E} = 103 \ (10) \qquad B_{D'} = 0.1228 \ (1)$$

$$B_E = 0.1336 \ (1) \qquad B_\beta = 0.1305 \ (10) \qquad \omega_\beta = 250 \ (1)$$

where all values are in cm^{-1} and the estimated errors are in units of the last quoted figure of the parameter.

The vibrational numbering proposed for the transitions analyzed in this work is dependent on the E-state assignments given by CL.[3] We computed Franck–Condon factors for the E–B transitions involved in the second step of CL's two-photon experiments using E-state constants from the present analysis and those for the well-known B state. Transitions to $v_E = 0$ were predicted to be weak. In an attempt to understand the source of the inconsistency, the dissociation energy of A$'$ relative to $v_{D'} = 0$ was estimated by fitting the five observed A$'$ term values to a near-dissociation expansion with the correct limiting slope for a R^{-5} potential (slope $= 0.0622$,[30,31] v at dissociation $\simeq 50$).[28,29] By combining the

dissociation energy found relative to $v_{D'} = 0$ with the known dissociation limit of A$'$,[32] an absolute term value for $v_{D'} = 0$ was obtained which was independent of the vibrational assignments in A$'$. The result was ≈ 900 cm^{-1} higher than that obtained from our deperturbation analysis and CL's $v_E = 0$ term value. This suggests that the level assigned by CL to $v_E = 0$ is actually $v_E \approx 3$, since ion-pair states of IF have vibrational frequencies of ≈ 250 cm^{-1}. As noted earlier, X-state v numbering was determined by including our own results with the precise X-state data for $v = 0$–19 and seeking a best fit as a function of v_X. When this procedure was repeated assuming $v_E = n$ instead of $v_E = 0$, a particularly good fit was obtained for $n = 2$ and an X-state numbering one less than previously estimated. This change in v_E would reduce our vibrational numbering in A$'$ by two.

At this time, the evidence is not strong enough to recommend a definite reassignment of CL's spectrum but should be regarded as starting point for future work.

IF provided the first example of an optically pumped heteronuclear electronic laser operating on the B–X transition in the red.[33-35] All the D$'$–A$'$ transitions analyzed in this work also exhibit gain,[5-12] and therefore the results of Tables I and II provide direct spectroscopic information on the laser transition.

Supplementary Material Available: Table of line frequencies and rotational assignments for the D$'$–A$'$ and E–X transitions analyzed in this work (9 pages). Ordering information is given on any current masthead page.

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