

FRANCK-CONDON FACTORS AND ABSOLUTE TRANSITION PROBABILITIES FOR THE IF ($B^3\Pi_{0+}-X^1\Sigma^+$) TRANSITION

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Abstract—Improved spectroscopic constants have been used to calculate Rydberg–Klein–Rees (RKR) potentials and Franck–Condon factors for the IF ($B^3\Pi_{0+}-X^1\Sigma^+$) transition. The Franck–Condon factors are generally in good agreement with previously calculated values, but differ by as much as 30% for transitions from higher levels of the B -state. Several experimentally measured relative transition moment functions have been evaluated and the best scaled, so that the total transition probability calculated for each B -state vibrational level, $A(v')$, matched measured values. The scaled function was then used to calculate individual transition probabilities, $A(v',v'')$, for the vibronic transitions.

1. INTRODUCTION

There is a renewed interest in the spectroscopy and kinetics of iodine monofluoride (IF), primarily as the lasing species in a chemical laser. Davis and Hanko¹ and Davis, Hanko and Shea² have observed lasing on the $B-X$ transition from several B -state rotational and vibrational levels using optical pumping of the B -state. Dlabal and Eden³ have used electrical discharges in NF_3/CF_3 I/He mixtures to induce lasing action on the $D'-A'$ transition. There are now several research groups working to find efficient chemical pumping agents for either the D' - or B -states.

The IF ($B^3\Pi_{0+}-X^1\Sigma^+$) transition was initially observed by Durie^{4,5} in an I_2-F_2 flame. He assigned the spectrum and produced the first spectroscopic constants. Clyne, Coxon, and Townsend⁶ observed a similar but more extensive band system in I-atom/F-atom/singlet oxygen mixtures. The ground state rotational constants were refined by Tiemann, Hoeft and Törting⁷ who measured the pure rotational spectrum. Birks, Gabelnick and Johnston^{8,9} observed chemiluminescence originating from both the $B-X$ and $A-X$ transitions in the reaction of I_2 with F_2 , calculated Franck–Condon factors for the $B-X$ transition, and measured the variation in the $B-X$ relative electronic transition moment with r -centroid. Clyne and McDermid¹⁰ recalculated the Franck–Condon factors for the $B-X$ transition using spectral parameters derived from Coxon's¹¹ reinterpretation of Durie's⁵ data. They also observed laser-induced fluorescence from the transition,¹² and measured the radiative lifetimes and apparent transition moments for B -state vibrational levels 0–9.¹³ More recently Trautmann, Trickl and Wanner,¹⁴ and Trickl and Wanner¹⁵ have reported improved spectroscopic constants for both the B - and X -states. Trickl and Wanner¹⁶ have also measured the variation in the relative transition moment for the $B-X$ transition over a wider range of vibrational levels.

In our studies of electronic energy transfer from N_2 ($A^3\Sigma_u^+$) and active nitrogen to the IF ($B^3\Pi_{0+}$) state, we found that there is still some confusion regarding the variation in the IF ($B^3\Pi_{0+}-X^1\Sigma^+$) transition moment with r -centroid, and that recent measurements of the spectroscopic constants for both the X - and B -states made possible a more accurate determination of the Franck–Condon factors for the transition. It is now also possible to calculate absolute transition probabilities for the $B-X$ system using information currently available in the literature. We have performed a new evaluation of the Franck–Condon factors and calculated transition probabilities as part of our present measurement program. These data are very useful for those engaged in kinetic studies of IF, and for those who wish to model the $B-X$ chemical laser system.

2. METHODS AND RESULTS

The determination of transition probabilities for the IF ($B^3\Pi_{0+} - X^1\Sigma^+$) transition starts with the calculation of accurate Rydberg–Klein–Rees (RKR) potentials for both the X - and B -states. A Numerov–Cooley routine is used to obtain numerical eigenfunctions and eigenvalues for each of the potentials, and the necessary overlap integrals are computed to provide Franck–Condon factors and r -centroids for the $B-X$ transition. The transition probabilities are then calculated using these Franck–Condon factors, the appropriate transition frequencies and molecular constants, and a scaled transition moment function. The scaling for the transition moment function is chosen so that the total transition probability for each B -state vibrational level agrees with the transition probability determined for that level from radiative lifetime measurements. The details of these procedures are discussed in the following sections.

2.1 RKR potentials

The RKR potentials for the X - and B -states were calculated using a fast quadrature method developed by Tellinghuisen.¹⁷ Dunham expansions of the form

$$G(v) = T_e + \sum_{l=1}^L C_l (v + \frac{1}{2})^l \quad (1)$$

and

$$B(v) = \sum_{p=0}^P C_p (v + \frac{1}{2})^p \quad (2)$$

were used to generate the vibrational and rotational term values, respectively. Expansion parameters determined by Trickl and Wanner¹⁵ were used to give vibrational term values for both the X - and B -states. The rotational constants of Durie⁵ were used in the X -state calculation while those of Tiemann, Hoelt and Törring⁷ were used for the B -state. These parameters accurately reproduce the vibronic band origins to within 0.02 cm^{-1} for a range of transitions comprising $v' \leq 11$ and $v'' \leq 17$. They are summarized in Table 1. The

Table 1. Dunham expansion parameters used to calculate RKR potentials for the IF B and X states. See text for references.

Term	IF($X^1\Sigma^+$)		IF($B^3\Pi_{0+}$)	
	C_l (cm^{-1})	C_p (cm^{-1})	C_l (cm^{-1})	C_p (cm^{-1})
1	610.22649	0.2797108	411.2759	0.22721
2	-3.12534	-1.8734(-3)	-2.85844	-1.398(-3)
3	-2.6139(-3)	-2.7(-6)	-6.2411(-2)	-8.2(-5)
4	-5.8379(-5)		--	
5			--	
6			-1.8331(-5)	
7			--	
8			--	
9			-1.0956(-8)	
10			--	
11			--	
12			9.255(-12)	
13			--	
14			--	
15			-3.8574(15)	

vibrational term values and classical turning points calculated for both electronic states are given in Table 2.

2.2 Eigenfunctions and Franck-Condon factors

Numerical eigenfunctions for vibrational levels up to 11 in the *B*-state and 17 in the *X*-state were calculated at 0.001 Å intervals using a Numerov-Cooley¹⁸ routine to solve the radial Schrödinger equation. Evaluations of the overlap integrals used to obtain Franck-Condon factors and *r*-centroids were done using Simpson's rule. The routines used 1000 uniformly spaced values of the potentials spanning a range of internuclear distance from 1.63 to 2.63 Å. The potential arrays were constructed from the RKR turning points using a 7-term interpolation polynomial. The attractive and repulsive regions of the potentials, which fall outside the range of the classical turning points, were evaluated by fitting the four closest turning points to the expressions

$$V(r) = D_e - c/r^d \quad (3)$$

for the attractive part, and

$$V(r) = a/r^{12} + b \quad (4)$$

for the repulsive part. In these expressions, D_e is the dissociation energy and a , b , c and d are adjustable parameters.

The computer routines and their inputs were verified by testing the eigenfunctions for proper normalization and orthogonality, and by comparing the calculated eigenvalues with those used to calculate the RKR potentials. The normalization and orthogonality of the eigenfunctions for each potential were tested by doing the overlap integrals for each eigenfunction of the potential with itself and with all of the other eigenfunctions of that potential. The diagonal elements in the resulting overlap integral arrays, which correspond to the overlap of each eigenfunction with itself, were unity to within 1 part in 10^7 . The off-diagonal elements in the arrays were not greater than 1.0×10^{-20} . Eigenvalues for the *X*-state, calculated using the Numerov-Cooley routine, agreed with those used in the RKR routine to within 0.03 cm^{-1} for the first 11 levels, and were different by no more than 8 cm^{-1} for

Table 2. Term values and classical turning points calculated by RKR inversion using the expansion parameters in Table 1.

Vibrational Level	IF($X^1\Sigma^+$)			IF($B^3\Pi_{0+}$)		
	E(cm^{-1})	$r_-(\text{Å})$	$r_+(\text{Å})$	E(cm^{-1})	$r_-(\text{Å})$	$r_+(\text{Å})$
0	304.332	1.8549	1.9708	204.916	2.0517	2.1930
1	908.299	1.8181	2.0197	610.272	2.0064	2.2527
2	1505.990	1.7943	2.0557	1009.345	1.9772	2.2972
3	2097.386	1.7759	2.0866	1401.739	1.9548	2.3361
4	2682.469	1.7606	2.1144	1787.011	1.9363	2.3720
5	3261.216	1.7474	2.1403	2164.615	1.9206	2.4064
6	3833.605	1.7357	2.1648	2533.882	1.9069	2.4399
7	4399.611	1.7252	2.1883	2893.609	1.8948	2.4733
8	4959.209	1.7156	2.2110	3242.523	1.8836	2.5070
9	5512.373	1.7068	2.2330	3578.471	1.8731	2.5419
10	6059.074	1.6987	2.2546	3898.045	1.8625	2.5790
11	6599.282	1.6911	2.2757	4193.911	1.8501	2.6214
12	7132.966	1.6840	2.2966			
13	7660.094	1.6773	2.3171			
14	8180.632	1.6710	2.3375		$r_e = 2.1190$	
15	8694.544	1.6650	2.3577			
16	9201.794	1.6593	2.3778			
17	9702.344	1.6539	2.3979			
		$r_e = 1.9098$				

levels up to 17. A similar comparison for the *B*-state showed agreement to within 0.2 cm^{-1} for the first 5 levels and a maximum deviation of 2.3 cm^{-1} for levels up to 11.

2.3 Transition moment and transition probabilities

The relative transition moment function spanning the widest range of *B*-state vibrational levels is given by Trickl and Wanner.¹⁶ Their analysis of IF (*B*-*X*) fluorescence from the reaction of F-atoms with I_2 , ICl and IBr yielded the function

$$|R_e(v', v'')|^2 \propto r(v', v'') - r_0(v'), \quad (5)$$

with

$$r_0(v') = r(v', 0) - (1 + 3.434 \times 10^{-5} v'^5)[r(v', 0) - 1.859 \text{ \AA}] \quad (6)$$

for $v' \leq 8$. We have modified their relative transition moment function to include a scaling parameter β such that the function becomes

$$|R_e(v', v'')|^2 = \beta \{r(v', v'') - r_0(v')\}, \quad (7)$$

and we can write the expression for the total transition probability for a given vibrational level

$$A(v') = \sum_{v''} A(v', v'') = (64\pi^4/3h)\beta \sum_{v''} \omega^3 |R_e(v', v'')|^2 |\langle q' | q'' \rangle|^2, \quad (8)$$

where ω is the transition frequency in cm^{-1} and $|\langle q' | q'' \rangle|^2$ is the Franck-Condon factor for the transition.

If all the transition frequencies and Franck-Condon factors from a given vibrational level are known, then a value of β can be chosen so that expression (8) produces the measured transition probability for that level. Our calculated Franck-Condon factors and the spectral parameters given above allow us to meet this criterion for levels 0-5 of the IF *B*-state. We have used the measured transition probabilities of Clyne and McDermid¹³ for transitions from IF *B*-state levels 0-9 to do a least-squares fit for the parameter β , such that the differences between the measured and calculated probabilities for levels 0-5 are minimized. The calculated and measured probabilities are given in Table 3 and Fig. 1. The calculated probabilities agree with those measured by Clyne and McDermid¹³ to within 7% for levels 0-5, and are nearly a linear function of vibrational level. A linear least-squares fit to the calculated probabilities, shown in Fig. 1, allows an extension of the calculated values for comparison with the full range of the measured data. In the extrapolated region

Table 3. Comparison of measured and fitted total transition rates for levels 0-9 of IF (*B*).

Vibrational Level	Measured $A(v')^a$	Fitted $A(v')^{a,b}$
0	1.44±0.10	1.54
1	1.49±0.07	1.48
2	1.42±0.12	1.43
3	1.45±0.06	1.38
4	1.34±0.11	1.34
5	1.23±0.06	1.27
6	1.21±0.06	1.22
7	1.16±0.05	1.17
8	1.16±0.07	1.12
9	1.14±0.12	1.07

^a 10^5 s^{-1} ; ^b Levels 6-9 extrapolated from calculated values for levels 0-5.

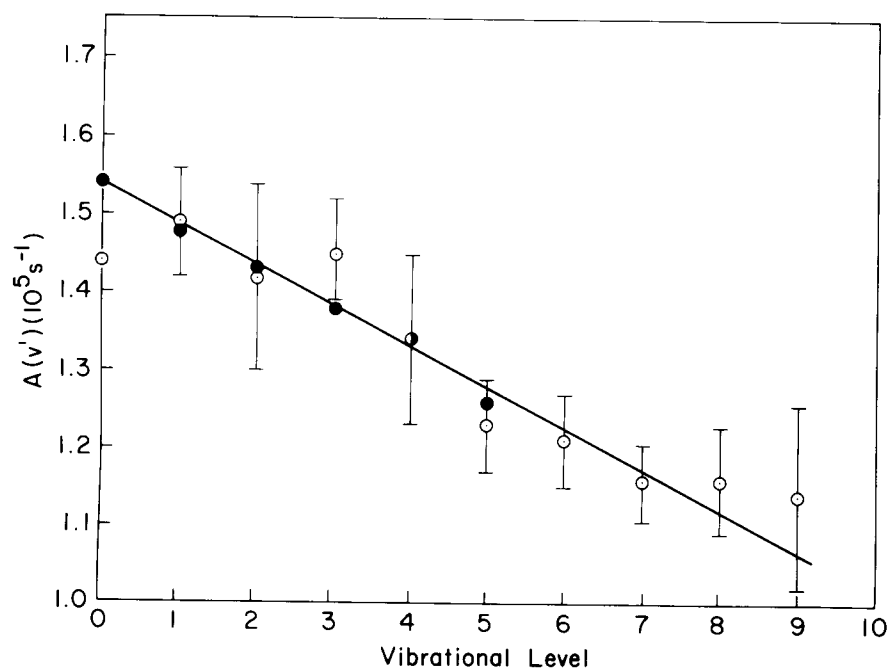


Fig. 1. Measured total transition rates (Ref. 13), \circ ; fitted total transition rates, \bullet ; and linear least-squares fit to fitted data, solid line, for IF (B) levels 0–9.

the agreement with the measured values is also quite good, and we have included the extrapolated values in Table 3.

The relative transition moment function of Trickl and Wanner¹⁶ can now be put on an absolute basis using the fitted value of β and is given as

$$|R_e(v', v'')|^2 = 0.445 \cdot [r(v', v'') - r_0(v')], \quad (9)$$

where the units are Debye,² and $r_0(v')$ has its previously defined value. Using the absolute transition moment function, our calculated Franck-Condon factors, and the known transition frequencies for the B - X transition, we can calculate transition probabilities for all transitions of interest. These probabilities, as well as the corresponding Franck-Condon factors and r -centroids, are given in Table 4 for transitions from B -state levels 0–9 to X -state levels 0–17.

3. DISCUSSION

Vibrational term values calculated for the X -state differ by as much as 1.3 cm^{-1} from those of Clyne and McDermid¹³ and 13 cm^{-1} from those of Gabelnick,⁸ whose results are summarized in Ref. 9. The corresponding classical turning points for these levels change by as much as 0.002 and 0.003 \AA , respectively. The term values calculated for the B -state using the new constants differ by 1 cm^{-1} from Clyne and McDermid¹³ and 3.2 cm^{-1} for Gabelnick.⁸ Classical turning points calculated from these term values differ by as much as 0.003 and 0.007 \AA , respectively. These changes are a direct result of the use of improved vibrational and rotational parameters. This improved accuracy enables us to compute the Franck-Condon factors to X -state level 17. The shifts in the potentials are not sufficient to affect significantly the Franck-Condon factors for transitions between levels with eigenfunctions having few nodes, but do result in large changes for transitions occurring between high levels in each manifold. For such transitions the present values differ by as much as 30% from previous results.

Extension of the Franck-Condon factor matrix to include X -state levels up to 17 gives us the full sum of the overlap integrals for B -state levels 0–4, and 95% of the sum for level 5. This procedure allows us to use these levels to determine the optimum value of β in the transition moment fitting routine. Previous calculations^{9,10} only determined the full overlap

Table 4. Franck-Condon factors, r centroids, and transition probabilities for IF (B_0-9) to IF (X_0-17). The figures in brackets are extrapolated values from Fig. 1. Exponents are in parenthesis.

v'' v'	0	1	2	3	4	5	6	7	8	9
0	4.952(-3) 2.007 6.97(2)	2.995(-2) 2.031 4.44(3)	8.638(-2) 2.055 1.32(4)	1.578(-1) 2.080 2.47(4)	2.046(-1) 2.106 3.22(4)	1.998(-1) 2.132 3.12(4)	1.522(-1) 2.158 2.33(4)	9.245(-1) 2.186 1.39(4)	4.546(-2) 2.215 6.62(3)	1.826(-2) 2.245 2.56(3)
1	2.288(-2) 1.991 3.06(3)	9.102(-2) 2.015 1.31(4)	1.498(-1) 2.038 2.25(4)	1.189(-1) 2.062 1.83(4)	3.166(-2) 2.085 4.90(3)	2.453(-3) 2.126 4.03(2)	6.417(-2) 2.142 1.01(4)	1.395(-1) 2.168 2.13(4)	1.564(-1) 2.195 2.33(4)	1.176(-1) 2.224 1.71(4)
2	5.505(-2) 1.975 6.88(3)	1.335(-1) 1.998 1.83(4)	9.772(-2) 2.021 1.41(4)	7.626(-3) 2.041 1.13(3)	2.983(-2) 2.073 4.68(3)	9.656(-2) 2.096 1.52(4)	6.666(-2) 2.119 1.04(4)	3.853(-3) 2.134 5.69(2)	2.771(-2) 2.180 4.28(3)	1.078(-1) 2.205 1.61(4)
3	9.227(-2) 1.960 1.08(4)	1.211(-1) 1.983 1.58(4)	1.764(-2) 2.004 2.44(3)	2.635(-2) 2.032 3.97(3)	8.467(-2) 2.054 1.30(4)	2.732(-2) 2.075 4.20(3)	8.289(-3) 2.111 1.35(3)	7.490(-2) 2.130 1.18(4)	6.828(-2) 2.154 1.05(4)	6.351(-3) 2.171 9.26(2)
4	1.216(-1) 1.946 1.33(4)	6.966(-2) 1.968 8.64(3)	3.761(-3) 1.998 5.39(2)	7.479(-2) 2.015 1.09(4)	2.889(-2) 2.036 4.35(3)	1.146(-2) 2.067 1.84(3)	7.009(-2) 2.087 1.11(4)	2.675(-2) 2.108 4.19(3)	7.428(-3) 2.148 1.21(3)	7.069(-2) 2.165 1.10(4)
5	1.348(-1) 1.931 1.38(4)	2.051(-2) 1.953 2.44(3)	4.066(-2) 1.978 5.52(3)	5.445(-2) 1.999 7.85(3)	1.526(-3) 2.035 2.50(2)	6.046(-2) 2.047 9.58(3)	2.194(-2) 2.067 3.47(3)	1.380(-2) 2.100 2.28(3)	6.392(-2) 2.120 1.03(4)	1.672(-2) 2.139 2.60(3)
6	1.314(-1) 1.918 1.32(4)	2.471(-4) 1.934 2.76(1)	6.787(-2) 1.963 9.20(3)	1.034(-2) 1.981 1.47(3)	3.745(-2) 2.010 5.90(3)	3.727(-2) 2.029 5.96(3)	5.475(-3) 2.061 9.33(2)	5.573(-2) 2.079 9.32(3)	9.825(-3) 2.096 1.59(3)	2.440(-2) 2.133 4.10(3)
7	1.163(-1) 1.904 1.17(4)	9.432(-3) 1.926 1.14(3)	5.943(-2) 1.950 8.29(3)	2.249(-3) 1.982 3.66(2)	5.430(-2) 1.994 8.73(3)	1.148(-3) 1.999 1.74(2)	4.402(-2) 2.040 7.56(3)	1.850(-2) 2.060 3.17(3)	1.662(-2) 2.091 2.93(3)	4.776(-2) 2.111 8.24(3)
8	9.543(-2) 1.891 9.64(3)	3.389(-2) 1.913 4.17(3)	3.042(-2) 1.938 4.39(3)	2.584(-2) 1.961 4.10(3)	2.927(-2) 1.979 4.82(3)	1.430(-2) 2.008 2.55(3)	3.871(-2) 2.024 6.84(3)	2.391(-3) 2.060 4.54(2)	4.576(-2) 2.072 8.30(3)	3.351(-3) 2.085 5.80(2)
9	7.411(-2) 1.878 6.63(3)	5.910(-2) 1.900 6.73(3)	6.184(-3) 1.929 8.86(2)	4.648(-2) 1.948 7.17(3)	3.124(-3) 1.961 4.86(2)	3.961(-2) 1.992 6.90(3)	6.469(-2) 2.004 1.10(3)	3.158(-3) 2.036 5.77(3)	1.692(-2) 2.053 3.03(3)	1.671(-2) 2.085 3.10(3)

V'	V''	10	11	12	13	14	15	16	17	Σ	τ_V'
0	6.027(-3)	1.642(-3)	3.708(-4)	6.956(-5)	1.086(-5)	1.413(-6)	1.535(-7)	1.403(-8)	1.000	1.000	6.49(-6)
	2.276	2.310	2.344	2.381	2.419	2.459	2.500	2.542	-		
	8.08(2)	2.10(2)	4.48(1)	7.92(0)	1.16(0)	1.39(-1)	1.40(-2)	1.17(-3)	1.54(5)		
1	6.514(-2)	2.781(-2)	9.389(-3)	2.546(-3)	5.607(-4)	1.011(-4)	1.497(-5)	1.839(-6)	1.000	1.000	6.76(-6)
	2.254	2.285	2.318	2.353	2.390	2.428	2.467	2.508	-		
	9.05(3)	3.69(3)	1.19(3)	3.04(2)	6.30(1)	1.06(1)	1.46(0)	1.65(-1)	1.48(5)		
2	1.462(-1)	1.189(-1)	6.754(-2)	2.864(-2)	9.398(-3)	2.440(-3)	5.089(-4)	8.588(-5)	1.000	1.000	6.99(-6)
	2.233	2.263	2.294	2.327	2.362	2.399	2.436	2.476	-		
	2.10(4)	1.64(4)	8.87(3)	3.57(3)	1.11(3)	2.71(2)	5.26(1)	8.24(0)	1.43(5)		
3	2.316(-2)	1.023(-1)	1.405(-1)	1.117(-1)	6.091(-2)	2.448(-2)	7.544(-3)	1.826(-3)	1.000	1.000	7.25(-6)
	2.218	2.243	2.272	2.303	2.336	2.371	2.408	2.446	-		
	3.48(3)	1.46(4)	1.91(4)	1.46(4)	7.52(3)	2.86(3)	8.25(2)	1.87(2)	1.38(5)		
4	5.957(-2)	2.804(-3)	3.165(-2)	1.104(-1)	1.363(-1)	9.938(-2)	4.986(-2)	1.842(-2)	0.993	0.993	7.46(-6)
	2.189	2.199	2.256	2.282	2.313	2.346	2.381	2.417	-		
	8.96(3)	3.88(2)	4.55(3)	1.50(4)	1.76(4)	1.22(4)	5.77(3)	1.99(3)	1.34(5)		
5	1.456(-2)	7.355(-2)	4.439(-2)	1.489(-6)	5.014(-2)	1.231(-1)	1.289(-1)	8.324(-2)	0.947	0.947	7.94(-6)
	2.180	2.201	2.225	3.298	2.294	2.323	2.356	2.390	-		
	2.34(3)	1.12(4)	6.48(3)	7.51(-1)	6.87(3)	1.59(4)	1.58(4)	9.57(3)	1.26(5)		
6	5.704(-2)	4.996(-3)	2.980(-2)	7.367(-2)	2.477(-2)	5.409(-3)	7.634(-2)	1.333(-1)	0.785	0.785	[8.20(-6)]
	2.153	2.165	2.214	2.237	2.261	2.317	2.335	2.366	-		
	9.24(3)	7.57(2)	4.66(3)	1.10(4)	3.49(3)	7.67(2)	9.96(3)	1.63(4)	[1.22(5)]		
7	8.182(-4)	4.001(-2)	4.266(-2)	5.655(-5)	5.015(-2)	6.368(-2)	6.828(-3)	2.438(-2)	0.598	0.598	[8.62(-6)]
	2.103	2.166	2.187	2.382	2.250	2.275	2.292	2.350	-		
	1.24(2)	6.73(3)	6.86(3)	1.27(1)	7.61(3)	9.15(3)	9.07(2)	3.24(3)	[1.16(5)]		
8	3.265(-2)	3.133(-2)	3.095(-3)	5.234(-2)	2.158(-2)	9.054(-3)	6.656(-2)	4.176(-2)	0.578	0.578	[9.01(-6)]
	2.124	2.143	2.194	2.200	2.220	2.269	2.288	2.313	-		
	5.89(3)	5.41(3)	5.60(2)	8.64(3)	3.37(3)	1.42(3)	9.71(3)	5.72(3)	[1.11(5)]		
9	3.463(-2)	1.167(-3)	4.404(-2)	1.114(-2)	1.955(-2)	5.133(-2)	3.667(-3)	3.162(-2)	0.497	0.497	[9.43(-6)]
	2.104	2.157	2.157	2.171	2.216	2.236	2.247	2.302	-		
	6.24(3)	2.27(2)	7.70(3)	1.82(3)	3.27(3)	8.06(3)	5.28(2)	4.59(3)	[1.06(5)]		

integral sum for levels 0 and 1, limiting the accuracy of any fit for the transition moment function.

There have been three determinations of the variation in the relative transition moment with r -centroid for the $B-X$ transition. The initial measurements of Birks, Gabelnick and Johnston⁹ showed a variation in the relative transition moment for transitions from B -state levels 0–2 characterized by the expression

$$|R_e(v', v'')|^2 \propto r(v', v'') - 1.859 \text{ \AA}. \quad (10)$$

The function varies by about a factor of three over the corresponding range of r -centroids. Subsequently, Clyne and McDermid¹³ inferred from their lifetime measurements that the transition moment varied by only about 10% for transitions originating from B -state levels 0–9. Recently Trickl and Wanner¹⁶ investigated the variation in the relative transition moment and reported a change with r -centroid previously given in expression (5) for transitions originating from B -state levels 0–8. Their transition moment function gives values of the transition moment which agree with those of Birks and co-workers⁹ where they overlap, and extends the range over which the transition moment is known.

We have determined that the apparent discrepancy between the transition moments of Clyne and McDermid¹³ and other measurements is due to a misinterpretation of the lifetime data by those authors. In reporting their transition moment values, Clyne and McDermid¹³ actually calculated the average transition moment for all transitions originating from a given B -state vibrational level. This quantity is given by the expression

$$R_e(v') = \frac{3h}{64\pi^4} \frac{A(v')}{\omega^{-3}(v')} \quad (11)$$

where

$$\omega^{-3}(v') = \sum_{v''} \omega(v', v'')^3 |\langle q'' | q'' \rangle|^2. \quad (12)$$

This average transition moment does vary by only about 10% for levels 0–9; however, this interpretation neglects the fact that the transition moment may vary significantly within any given vibronic progression while having the same average value relative to other progressions in the system.

The data of Clyne and McDermid¹³ are consistent with other measurements of the relative transition moment if viewed more closely. The quantity $3\sqrt{\omega^{-3}(v')}$, which is the Franck–Condon weighted average transition frequency for a vibronic progression, varies only slightly for progressions originating from B -state levels 0–9. Since $B-X$ emission occurs almost entirely at the classical turning points, transition frequencies can be associated with the r -centroids for those transitions. A plot of transition frequency vs r -centroid is approximately linear, and the average transition frequencies of Clyne and McDermid¹³ and can be assigned corresponding r -centroids from this plot. When these r -centroids are used in the relative transition moment function of Birks, Gabelnick and Johnston,⁹ this function gives both the same sign and magnitude of the variation in average transition moment observed by Clyne and McDermid.¹³ Hence, all of the data sets are consistent and we feel confident to use the more extensive relative transition moment function of Trickl and Wanner.¹⁶

We have done a linear propagation of errors analysis for our computation of the transition probabilities. This analysis included a 10% uncertainty in the transition moment and a 5% uncertainty in the Franck–Condon factors. The total uncertainty in the transition probabilities is estimated to be 10% for strong transitions, and as great as 30% for weaker transitions. We have used these transition probabilities in a linear least-squares spectral fitting routine. In Fig. 2 we show the spectrum of IF ($B-X$) emission, excited by energy transfer from N_2 (A) (light line) at 5 Torr total pressure of Ar buffer. Some emission from

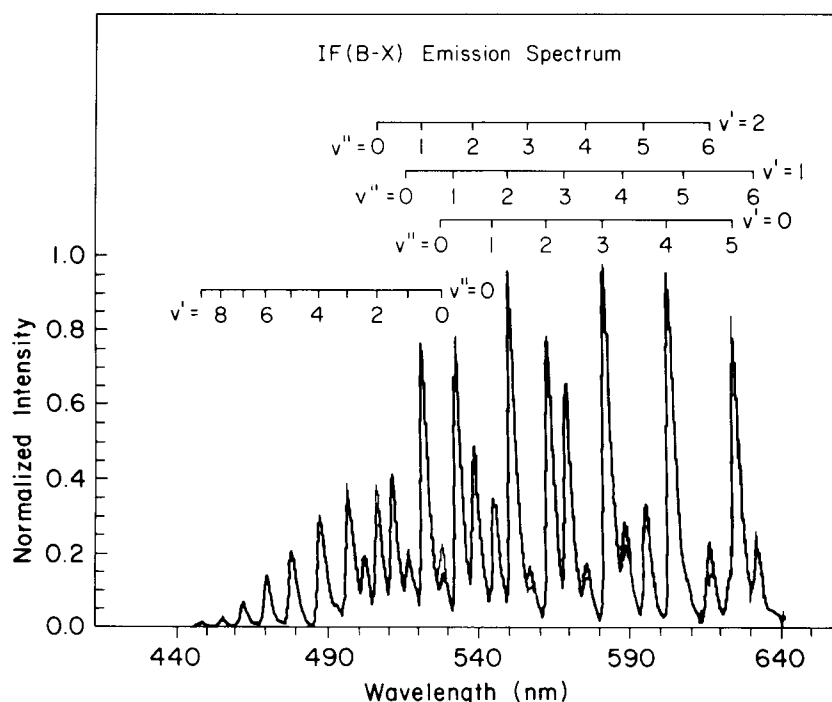


Fig. 2. IF ($B-X$) emission spectrum excited by N_2 (A) energy transfer (light line) and least-squares fit to data using calculated transition probabilities (dark line).

NF ($b^1\Sigma^+ - X^3\Sigma^-$) lies under the 0-0 band. The least-squares fit to the spectrum is shown as the darkened line in the figure. The accuracy of the transition probabilities is demonstrated by the good fits to the long progressions originating in $v' = 0-2$. Over the range of these progressions, the transition moment varies by approximately a factor of two, while the spectral fits match the observed spectra to within 15%. If the transition moment were invariant with r centroid, a much larger error would be observed in the spectral fit.

While there have been no other determinations of transition probabilities for this system, the transition probabilities reported here are at least in qualitative agreement with the stimulated emission data reported by Davis, Hanko and Shea.² Our calculations would predict strong emission from the 1-8, 2-10, 3-11, 3-12, 4-0 and 5-11 bands, in agreement with their low-pressure optical pumping experiments. We would also predict lasing on the 0-5 band relative to the 0-4 band, when the probabilities are converted to stimulated emission coefficients. Clyne and McDermid¹³ showed that radiative lifetimes for $4 < J' < 50$ in each of B -state levels 0-8 are essentially equal. Work on Franck-Condon factors for I_2 have shown little variation with rotational quantum number except in highly rotationally excited species.¹⁹ Thus we might expect to see little variation in these transition probabilities with rotational quantum number aside from the usual Hönl-London line-strength factor.

4. CONCLUSIONS

Franck-Condon factors for the IF ($B-X$) transition calculated using improved spectroscopic constants differ negligibly from previously calculated values for transitions originating from low levels of the B state. For transitions originating from higher levels of the B state, which are most affected by the use of improved spectroscopic constants, the newly calculated values differ by as much as 30% from prior results.^{9,10} We have resolved the discrepancy between previously reported variations in the relative transition moment by a reinterpretation of the results of Clyne and McDermid,¹³ resulting in three consistent sets of data. The relative transition moment function of Trickl and Wanner¹⁶ has been scaled so that calculated total transition probabilities match measured values.¹³ Calculated probabilities for individual $B-X$ transitions using the scaled function are consistent with ob-

servations of lasing on strong transitions originating from the outer turning point of the *B*-state potential.

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