

Theoretical study of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ band systems of S_2

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Abstract

Multireference configuration-interaction (MRCI) wavefunctions and potential energy curves have been calculated for the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, and $B''^3\Pi_u$ states of S_2 using correlation consistent Gaussian basis sets. These wavefunctions are utilized to compute the transition dipole moments of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ systems. Oscillator strengths, transition probabilities, and radiative lifetimes are computed for the B–X and B''–X systems and comparison is made with experimental data.

1. Introduction

The $B^3\Sigma_u^- - X^3\Sigma_g^-$ band system has been the subject of numerous experimental studies in the last two decades and has recently been observed in absorption in the aftermath of the comet Shoemaker-Levy 9 impact with Jupiter [1]. The B–X transition of S_2 has also been observed in cometary atmospheres [2,3] and S_2 is believed to play an important role in the sulfur chemistry of dense molecular clouds [4,5]. In emission, the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition is the source of continuous visible radiation recently demonstrated in microwave excited sulfur discharge lamps [6].

Previous experimental investigations of S_2 include the recent study by Lindner et al. [7] on the B–X transition using laser excitation spectroscopy providing molecular constants for the $X^3\Sigma_g^-$ ground state and low-lying vibrational levels of the $B^3\Sigma_u^-$ state. They noted strong perturbations for high-lying rovibrational levels of the $B^3\Sigma_u^-$ state. Heaven et al. [8] performed a detailed rotational analysis of a laser in-

duced fluorescence (LIF) spectrum of the 2–3 transition of the B–X band. Bondybey and English [9,10] conducted matrix isolation studies of S_2 fluorescence, the perturbations in the spectra, and relaxation processes involving the B–X system. Patino and Barrow [11] in laser excitation fluorescence experiments studied the B–X system in detail and in a deperturbation analysis also derived constants for the $B''^3\Pi_u$ state. Quick and Weston [12] measured fluorescence lifetimes for the B–X transition in the wavelength range of 280–315 nm and, in addition, observed much longer low-intensity lifetime peaks throughout the absorption spectrum. Anderson et al. [13] utilized laser excitation to specific rotational levels of the $B^3\Sigma_u^-$ state and measured emission intensity to determine Franck–Condon factors.

S_2 has been studied theoretically by Swope et al. [14] using self-consistent-field (SCF) and configuration interaction (CI) methods with double-zeta quality basis sets. Swope et al. [14] predicted the presence of an unbound $^1\Pi_u$ state approximately 37600

cm^{-1} above the ground state. The ${}^1\Pi_u$ state is believed to be responsible for the predissociation of high-lying ($v' \geq 9$) ro-vibrational levels of the $B^3\Sigma_u^-$ state [12]. To our knowledge, no previous calculations of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ or $B''^3\Pi_u - X^3\Sigma_g^-$ transition moments have been reported. This Letter focuses on calculations of the electronic transition dipole moments between the $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states and the $X^3\Sigma_g^-$ and $B''^3\Pi_u$ states.

2. Methods

The calculations utilize the augmented correlation consistent Gaussian basis sets (aug-cc-pViZ, $3 \leq i \leq 5$) of Dunning and co-workers [15].

We performed multireference configuration-interaction (MRCI) calculations utilizing complete active space SCF (CASSCF) orbitals. Internal contraction (IC) was utilized to keep the size of the calculations manageable and all the calculations were performed in D_{2h} symmetry.

The principal occupations of the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, and $B''^3\Pi_u$ states are

$$X^3\Sigma_g^- \dots 5\sigma_g^2 2\pi_u^4 2\pi_g^2, \quad (1)$$

$$B^3\Sigma_u^- \dots 5\sigma_g^2 2\pi_u^3 2\pi_g^3, \quad (2)$$

$$B''^3\Pi_u \dots 5\sigma_g^2 2\pi_u^4 2\pi_g 5\sigma_u, \quad (3)$$

respectively. The initial active space in the CASSCF calculations was composed of the $4-5\sigma_g$, $2\pi_u$, $2\pi_g$, and $4-5\sigma_u$ orbitals corresponding to the 3s and 3p sulfur valence orbitals with twelve electrons active.

We performed a series of single state ICMRCI calculations to determine the dissociation energy of each electronic state. The ICMRCI calculations utilized the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets with the same active space as in the CASSCF calculations in order to calibrate the effect of basis set enlargement on the dissociation energies of all electronic states. The effects of higher-order excitations are accounted for by using the multireference analog of the Davidson correction (denoted +Q). We extrapolated the ICMRCI+Q results to the complete basis set (CBS) limit assuming that the energy improvement with basis set extrapolation is logarithmic [16].

For the transition moment calculations, we utilized the aug-cc-pV5Z basis set. We found it necessary to include an additional π_u orbital for the proper description of the transition moment. The enlarged active space in the transition moment calculations therefore consisted of the $4-5\sigma_g$, $2-3\pi_u$, $2\pi_g$, and the $4-5\sigma_u$ orbitals. The orbitals for the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition moment computation were obtained from a state-averaged (SA) CASSCF calculation of the $X^3\Sigma_g^-$, ${}^3\Delta_u$, and $B^3\Sigma_u^-$ states. Similarly, the orbitals for the $B''^3\Pi_u - X^3\Sigma_g^-$ transition moment computation were obtained from a SA CASSCF calculation of the $X^3\Sigma_g^-$ and $B''^3\Pi_u$ states. Calibration calculations were performed to investigate the effect of active space enlargement on the transition moment. The ICMRCI calculations utilized the same active space described in the CASSCF calculations above with the sulfur 1s, 2s, and 2p orbitals uncorrelated. Within the Franck-Condon regions of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ transitions, the enlarged active space calculations that included the additional π_u orbital resulted in values for the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ transition moments that were on average 9% smaller and 15% larger, respectively, than SA calculations without the π_u orbital.

All states exhibited significant Rydberg behaviour at nuclear separations shorter than $2.80 a_0$; this was observed by adding additional diffuse s type functions to our basis sets. The addition of diffuse s type functions did not affect our results for the calculation of potential curves or transition moments for nuclear separations beyond $3.0 a_0$. Since the Franck-Condon regions for both the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ transitions lie well beyond $3.0 a_0$, the Rydberg character would not affect our computed lifetimes. All calculations were performed using MOLPRO-94 [17].

3. Results

The potential curves derived from ICMRCI+Q results for the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, and $B''^3\Pi_u$ states are shown in Fig. 1. Spectroscopic constants are computed by numerically integrating the radial nuclear Schrödinger equation to solve for low lying rotational $0 \leq J \leq 5$ and vibrational $0 \leq v \leq 5$ levels [18]. The computed energy levels were fit to an expression

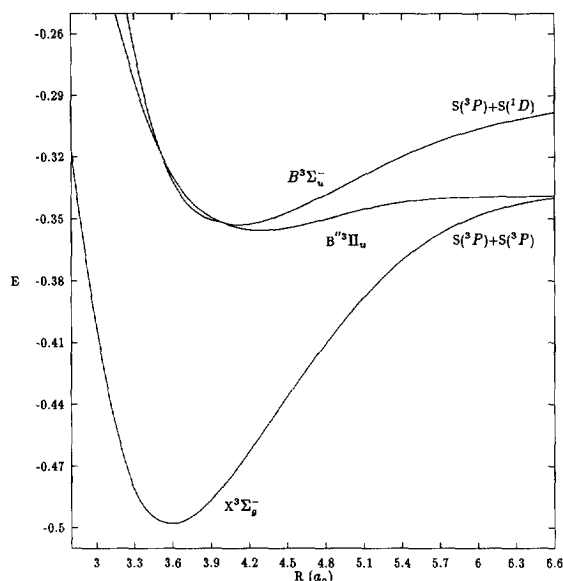


Fig. 1. Theoretical potential curves for the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states of S_2 . Units are in au with respect to -795.0 .

for the ro-vibrational energies of the form

$$E(v, J) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + [B_e - \alpha_e(v + 1/2)](J(J + 1) - \Omega^2), \quad (4)$$

where Ω is the projection of the total nuclear angular momentum on the internuclear axis.

The computed spectroscopic constants for the single state ICMRCI+Q calculations are given in Table 1 and compared with the available experimental data. Good agreement is found between our computed values and experimental values for the spectroscopic constants of the $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states. The use of spectroscopic constants determined from ICMRCI+Q calculations using SA CASSCF orbitals (optimized for transition moment calculations) slightly reduced the agreement with experimental values in comparison to results based on ICMRCI+Q single state calculations.

From the ICMRCI+Q results, we obtain a dissociation energy for the $X^3\Sigma_g^-$ state in the CBS valence one-particle limit that is 0.0086 eV larger than that computed with the cc-pV5Z basis set. Similarly, the CBS limits of the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states are 0.0225 and 0.0080 eV larger, respectively. The estimated errors for the computed dissociation energies were obtained by considering the error in the CBS limit extrap-

olation, which was determined by varying the slope obtained from the extrapolation by $\pm 50\%$. Basis set superposition errors are less than 4.6×10^{-4} eV in each case. Additional errors (such as incompleteness of the n-particle space and correlation of inner shells) in the ab initio values for the dissociation energies are anticipated to be small since the CBS extrapolated values are in close agreement with the experimental values.

The experimental value for the dissociation energy of the $X^3\Sigma_g^-$ state was determined using values for heats of formation of S_2 and atomic sulfur from the JANAF thermochemical data tables [19,20]. The experimental values reported for the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states also utilized the experimental T_e values [11,22] and the $S(^3P-^1D)$ experimental splitting [23].

The agreement between our values and those calculated by Patino and Barrow [11] for the spectroscopic constants of the $B''^3\Pi_u$ state is not as good as the agreement with experiment for the $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states but is still reasonable considering that Patino and Barrow [11] described their results for the $B''^3\Pi_u$ state as tentative. Patino and Barrow's [11] result for the dissociation energy of the $B''^3\Pi_u$ state (0.611 eV) is inconsistent with both our result (0.516 eV) and the computed value based on their own experimental result for T_e and the experimental value for the dissociation energy of the $X^3\Sigma_g^-$ state.

The transition dipole moments for the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ transitions are given in Table 2. For the computation of band transitions and oscillator strengths we utilized the experimental spectroscopic constants in Table 1 to construct potentials of the form

$$V(R) = -D_e \left(1 + \sum_{i=1}^3 a_i \rho^i \right) \exp(-a_1 \rho),$$

where $\rho = R - R_e$, and the coefficients a_i ($1 \leq i \leq 3$) are determined from analytic derivatives [24] which are the coefficients of the Taylor expansion of the energy about the minimum of the potential [25,26]. Franck-Condon factors for the $B^3\Sigma_u^-$ were calculated and found to be in good agreement with the experimental values of Anderson et al. [13]. Using these deduced experimental potential curves the crossing point of the potential curves of the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states is determined to be 4.077 a_0 as compared to 4.069

Table 1

Spectroscopic constants for the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, and $B''^3\Pi_u$ states derived from single state ICMRCI+Q calculations

		r_e (a_0)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	T_e (eV)	D_e^a (eV)
$X^3\Sigma_g^-$	this work	3.583	719.8	2.81	0.2927	0.00148	–	4.392 ± 0.03
	exp. ^{b,c}	3.570	725.7	2.844	0.2955	0.00157	–	4.410 ± 0.008
	Ref. [21]	3.591	718.5	2.84	0.292	0.0016	–	4.323
$B^3\Sigma_u^-$	this work	4.103	434.0	2.54	0.2234	0.00198	3.946	1.585 ± 0.04
	exp. ^c	4.101	434.0	2.750	0.2239	0.0023	3.947	1.608 ± 0.008
$B''^3\Pi_u$	this work	4.311	325.4	4.52	0.2026	0.00261	3.875	0.516 ± 0.04
	exp. ^d	4.35	335.2	4.5	0.199	0.0028	3.852	0.611
	exp. ^e							0.5577 ± 0.010

^a Theoretical dissociation energies computed in the CBS limit (see text). Experimental dissociation energies computed from Refs. [19] and [20].^b Ref. [7]. ^c Ref. [22]. ^d Ref. [11].^e Obtained using T_e ($B''-X$) and the experimental D_e of the ground state.

Table 2

The ICMRCI transition dipole moments (au) for $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B''^3\Pi_u - X^3\Sigma_g^-$ transitions (nuclear separation R in a_0)

$B^3\Sigma_u^- - X^3\Sigma_g^-$		$B''^3\Pi_u - X^3\Sigma_g^-$	
R	transition moment	R	transition moment
2.85	0.2124	2.90	0.3280
2.90	0.3291	3.20	0.1942
3.00	0.5237	3.36	0.1225
3.16	0.7221	3.50	0.0874
3.30	0.8280	3.64	0.0682
3.50	0.9106	3.80	0.0569
3.60	0.9301	3.90	0.0533
3.70	0.9384	4.00	0.0512
3.90	0.9297	4.20	0.0495
4.10	0.8970	4.40	0.0493
4.30	0.8487	4.60	0.0491
4.50	0.7890	4.70	0.0489
4.80	0.6803	4.84	0.0483
5.10	0.5461	5.00	0.0471
5.40	0.3922	5.24	0.0444
5.70	0.2439	5.50	0.0404
6.00	0.1330	6.00	0.0318
6.50	0.0437	6.50	0.0234
7.00	0.0156	7.00	0.0169

 a_0 for the curves determined from the state averaged calculations described above.The absorption oscillator strength from a vibrational level v'' of the X state to a v' level of an excited elec-tronic state is given by $gf_{v''v'}$ where g is a degeneracy factor and the $f_{v''v'}$ value is given by

$$f_{v''v'} = \frac{2}{3} \Delta E_{v'v''} |D_{v'v''}|^2, \quad (5)$$

where

$$D_{v'v''} = \langle \chi_{v'}(R) | D(R) | \chi_{v''}(R) \rangle \quad (6)$$

is the vibrationally averaged electronic transition dipole moment in atomic units, $\Delta E_{v'v''}$ is the transition energy, and $\chi_v(R)$ is the radial nuclear wavefunction obtained by numerically integrating the radial nuclear Schrödinger equation [18]. The $f_{v''v'}$ values for absorption into the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states from the $X^3\Sigma_g^-$ state are given in Tables 3 and 4.The degeneracy factor g needed to compute the absorption oscillator strength is equal to 1 for a $\Sigma \rightarrow \Sigma$ transition ($X \rightarrow B$) and equal to 2 for a $\Sigma \rightarrow \Pi$ transition ($X \rightarrow B''$).The probability of spontaneous emission from a vibrational level v' of an upper electronic state to a discrete bound vibrational level v'' of the $X^3\Sigma_g^-$ state is given by

$$A_{v'v''} = 6.67023 \times 10^{-1} \nu_{v'v''}^2 f_{v'v''} \text{ s}^{-1}, \quad (7)$$

with $\nu_{v'v''}$ being the transition frequency in cm^{-1} . Similarly, the probability of spontaneous emission from an upper vibrational level v' of the $B^3\Sigma_u^-$ elec-

Table 3

The $f_{v''v'}$ values (Eq. (5)) for the $B^3\Sigma_u^- - X^3\Sigma_g^-$ transition. The absorption oscillator strengths are equal to the $f_{v''v'}$ values for the $X \rightarrow B$ transition

v'	$f_{v''v'} (\times 10^{-3})$									
	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$	$v'' = 8$	$v'' = 9$
0	0.00	0.02	0.14	0.54	1.52	3.29	5.69	8.06	9.54	9.61
1	0.01	0.14	0.71	2.21	4.69	7.07	7.59	5.48	2.15	0.10
2	0.05	0.47	1.93	4.60	6.86	6.26	2.85	0.14	0.98	3.74
3	0.15	1.12	3.62	6.31	5.95	2.27	0.00	1.97	4.25	2.86
4	0.33	2.07	5.19	6.24	2.93	0.02	1.91	4.04	1.93	0.00
5	0.63	3.22	6.05	4.48	0.47	1.11	3.80	1.99	0.02	2.23
6	1.06	4.33	5.87	2.15	0.13	3.10	2.73	0.03	1.86	2.87
7	1.60	5.20	4.77	0.45	1.45	3.51	0.61	0.96	2.97	0.65
8	2.21	5.64	3.17	0.01	2.90	2.17	0.06	2.61	1.48	0.19
9	2.86	5.59	1.62	0.66	3.35	0.58	1.20	2.54	0.06	1.77
10	3.48	5.10	0.51	1.77	2.67	0.00	2.43	1.11	0.54	2.37
11	4.05	4.30	0.03	2.69	1.45	0.58	2.53	0.07	1.84	1.22
12	4.51	3.34	0.12	3.06	0.41	1.61	1.61	0.28	2.24	0.10
13	4.86	2.37	0.62	2.82	0.00	2.32	0.52	1.26	1.45	0.26
14	5.08	1.50	1.28	2.16	0.23	2.34	0.01	2.00	0.40	1.23
15	5.18	0.82	1.92	1.35	0.84	1.77	0.24	1.98	0.00	1.86
16	5.16	0.34	2.38	0.64	1.51	0.97	0.90	1.32	0.40	1.61
17	5.05	0.08	2.62	0.18	1.96	0.32	1.54	0.54	1.13	0.83
18	4.86	0.00	2.62	0.00	2.10	0.02	1.84	0.06	1.63	0.16
19	4.61	0.07	2.42	0.09	1.93	0.08	1.73	0.05	1.62	0.02
20	4.32	0.25	2.10	0.35	1.55	0.40	1.31	0.41	1.20	0.36

tronic state to the vibrational continuum of the $X^3\Sigma_g^-$ state k'' is given by

$$A_{v'k''}(\lambda) = 9.232 \times 10^{20} |D_{v'k''}|^2 / \lambda^5 \text{ s}^{-1} \text{ \AA}, \quad (8)$$

where k'' is the wavenumber for the relative nuclear motion in the final state, λ is the wavelength of the radiative transition in \AA, and

$$D_{v'k''} = \langle \chi_{v'}(R) | D(R) | \chi_{k''}(R) \rangle \quad (9)$$

is the electronic transition dipole moment averaged over the bound level v' of the upper electronic state and continuum level k'' of the lower electronic state in atomic units. The continuum radial wavefunction is normalized so that it has the asymptotic form

$$\chi_{k''}(R) = \frac{2\mu}{\pi \hbar^2 k''} \sin(k''R + \delta), \quad (10)$$

where μ is the reduced mass and δ is the elastic scattering phase shift.

The total probability of spontaneous radiative decay is given by

$$A_{v'} = \sum_{v''} A_{v'v''} + \int_{\lambda_f}^{\infty} A_{v'k''}(\lambda) d\lambda, \quad (11)$$

where λ_f is the transition for which $k'' = 0$. The radiative lifetime is the inverse of the total decay probability ($\tau_{v'} = 1/A_{v'}$). For levels of the $B^3\Sigma_u^-$ state ($v' \geq 10$) lying in the continuum of the $X^3\Sigma_g^-$ state, the contribution of the continuum transition probability to the total spontaneous transition probability is less than 0.4% in all cases.

For the rotational portion of the radial nuclear Hamiltonian, we took $J = 1$ and $\Omega = 0$ for both the $B^3\Sigma_u^-$ and $X^3\Sigma_g^-$ states and $J = 2$ and $\Omega = 0$ for the $B''^3\Pi_u$ state. The results computed in this Letter for spontaneous decay lifetimes should therefore be approximately equal to those for rotational levels lying close to the observed bandheads for the B–X and B''–X transitions.

The radiative decay lifetimes for the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states are given in Table 5. The theoretical val-

Table 4

The $f_{v''v'}$ values (equation 5) for the $B''^3\Pi_u-X^3\Sigma_g^-$ transition. The absorption oscillator strengths are twice the $f_{v''v'}$ values for the $X\rightarrow B''$ transition

v'	$f_{v''v'} (\times 10^{-3})$									
	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$	$v'' = 8$	$v'' = 9$
0	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.23	0.63	1.44
1	0.00	0.00	0.00	0.01	0.03	0.14	0.46	1.24	2.81	5.35
2	0.00	0.00	0.00	0.03	0.14	0.50	1.46	3.39	6.38	9.72
3	0.00	0.00	0.01	0.09	0.39	1.27	3.19	6.27	9.59	11.2
4	0.00	0.00	0.04	0.22	0.86	2.49	5.40	8.82	10.7	8.68
5	0.00	0.01	0.09	0.45	1.59	4.05	7.51	9.94	8.82	4.27
6	0.00	0.02	0.17	0.80	2.56	5.70	8.87	9.22	5.46	0.90
7	0.00	0.04	0.30	1.28	3.66	7.09	9.15	7.09	2.23	0.03
8	0.00	0.07	0.47	1.87	4.76	7.97	8.33	4.42	0.35	1.19
9	0.01	0.11	0.69	2.51	5.72	8.21	6.75	2.09	0.06	2.96
10	0.01	0.16	0.95	3.15	6.41	7.83	4.85	0.59	0.88	4.15
11	0.02	0.23	1.23	3.73	6.77	6.97	3.05	0.02	2.07	4.29
12	0.03	0.30	1.51	4.20	6.80	5.81	1.61	0.17	3.04	3.59
13	0.03	0.37	1.76	4.52	6.51	4.57	0.66	0.71	3.49	2.49
14	0.04	0.44	1.95	4.65	5.99	3.39	0.16	1.33	3.42	1.43
15	0.05	0.49	2.08	4.61	5.30	2.37	0.00	1.82	2.99	0.65
16	0.05	0.53	2.13	4.39	4.53	1.58	0.05	2.09	2.38	0.20
17	0.06	0.54	2.07	4.01	3.74	0.99	0.19	2.11	1.76	0.02
18	0.06	0.52	1.91	3.49	2.96	0.59	0.31	1.94	1.21	0.00
19	0.05	0.46	1.63	2.85	2.23	0.33	0.38	1.61	0.79	0.04
20	0.04	0.36	1.24	2.09	1.53	0.17	0.35	1.18	0.47	0.08

Table 5

Radiative decay lifetimes for $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states

$B^3\Sigma_u^-$			$B''^3\Pi_u$	
v'	$\tau_{v'} \text{ (ns)}$	experiment ^a	v'	$\tau_{v'} \text{ (}\mu\text{s)}$
0	37.0		0	25.5
1	37.7		1	25.9
2	38.4	33.4 (2.8)	2	26.4
3	39.0	34.6 (2.9)	3	27.0
4	39.7	36.0 (3.8)	4	27.6
5	40.4	36.5 (2.0)	5	28.3
6	41.1	34.6 (3.4)	6	29.1
7	41.8	33.2 (2.8)	7	30.0
8	42.5	42.0 (4.2)	8	31.0
9	43.2	40	9	32.2
10	44.0	$\leq 3^b$	10	33.6
11	44.8		11	35.3

^a Ref. [12]. Values in parentheses are stated errors.

^b Onset of predissociation.

ues are in good agreement with the experimental values obtained by Quick and Weston [12] using LIF excitation, given the stated errors in the experimental

values and the estimated 10% uncertainty in the theoretical values.

Meyer and Crosley [27] report a value of 36 ns for high rotational levels ($J' = 41-43$) of the $v' = 3, 4$ vibrational levels of the $B^3\Sigma_u^-$ state which agrees with our values. However, they also report a value of 20 ns for the $v' = 3, J' = 13$ level and ascribe the reduction of the lifetime for the lower rotational level to a perturbation. The perturbation suggested must be due to the $B''^3\Pi_u$ state and as the calculated theoretical lifetimes for ro-vibrational levels of the $B''^3\Pi_u$ states are much greater (Table 5), this perturbation would necessarily lead to a lengthening of the lifetimes for the $B^3\Sigma_u^-$ state. We therefore conclude that the 20 ns lifetime reported by Meyer and Crosley [27] is inconsistent with our results and the experimental results of Quick and Weston [12].

Bondybey and English [10] reported considerably longer lifetimes (~ 200 ns) than those for B-X radiative emission for their excitation spectra of S_2 in an argon matrix, which they attribute to $B''^3\Pi_u-X^3\Sigma_g^-$ emission. Quick and Weston [12] also reported low

intensity long-lived emission at wavelengths shortward of the higher intensity emission identified with the B–X bandhead. Based upon quenching experiments in which they observed the rise time of fluorescence signals, they assigned this long lived emission to the $B^3\Pi_u$ state and obtained a lifetime of approximately 350 ns. Our results for the radiative lifetime of a pure $B^3\Pi_u$ state indicate that Quick and Weston's [12] observation of a 350 ns lifetime corresponds to a mixed state consisting primarily of $B^3\Pi_u$ character with an admixture (approximately 10%) of the $B^3\Sigma_u^-$ emission.

Quick and Weston [12] reported an approximate result of 3 ns or less for the lifetime of the $v' = 10$ level of the $B^3\Sigma_u^-$ state which was observed to be weak in emission. Since the expected radiative lifetime is 43.7 ns, this indicates significant non-radiative decay and the onset of predissociation by the $^1\Pi_u$ state. Absorption experiments by Olsson [28] also showed slight line broadening for the $v' = 10$ level and much greater broadening for levels $v' \geq 11$. Using our value for the radiative lifetime of the $v' = 10$ level and Quick and Weston's value of ≤ 3 ns for the actual lifetime, we find the non-radiative broadening for the $v' = 10$ level of the $B^3\Sigma_u^-$ state to be approximately 0.0016 cm^{-1} .

4. Summary

We have computed transition moments, absorption oscillator strengths, and radiative lifetimes for the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $B^3\Pi_u - X^3\Sigma_g^-$ transitions of S_2 and found the radiative lifetimes of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ system agree well with experiment [12]. The long lived emission observed in previous experiments [10,12] is due to emission from the $B^3\Pi_u$ state with an admixture of perturbative $B^3\Sigma_u^-$ character.

The higher-lying ro-vibrational levels ($v \geq 10$) of the $B^3\Sigma_u^-$ state are predissociated with the likely mechanism being spin-orbit coupling with the $^1\Pi_u$ state. Future work will focus on perturbations influencing the $B^3\Sigma_u^-$ and $B^3\Pi_u$ states as well as the crossing and predissociation of high lying ro-vibrational levels ($v \geq 10$) of the $B^3\Sigma_u^-$ state by the $^1\Pi_u$ state.

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