Theoretical study of the energies and lifetimes of the low-lying states of bismuth fluoride

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A series of CI calculations has been carried out for various low-lying electronic states of the bismuth fluoride molecule by employing relativistic effective core potentials including spin–orbit effects. It is found that the lowest 0^+ excited state ($A0^+$) of this system contains a large contribution from the $\pi^* \rightarrow \sigma^* \, ^3\Pi$ λ–s state, especially at bond distances which are equal to or greater than the equilibrium value for the $X_1 0^+$ ground state. The $B0^+$ state at somewhat higher energy is found to contain the largest portion of the $b \, ^1\Sigma^+$ character arising from the $\pi^4 \pi^{*2}$ configuration, in disagreement with earlier calculations by Balasubramanian who only reports a single excited state of this (0^+) symmetry. Results of the latter study for the $X_1 0^+$, $X_2 1$ and $a2$ states of lower energy are in good agreement with those of the present work, however. The relatively large r_e value observed for the $A0^+$ state is quite consistent with the present theoretical description, as well as the correspondingly lower vibrational frequency compared to that of $X_1 0^+$. Radiative lifetimes have also been obtained for a number of excited states and the results are found to be in reasonably good agreement with recent measured data. An explanation is also provided for the anomalous μ_0/μ_1 ratio for the $A0^+ \rightarrow X$ transitions, again based on the large amount of $^3\Pi$ character in the upper state. The present data also provide a clear assignment for the A' and A" states recently found for this system ($\Omega = 1$ and 0^-) respectively. The lifetime of the $X_2 1$ state is computed to be 1.05 ms and a zero-field splitting of 6937 cm^{-1} is obtained, both of which results are in good agreement with the corresponding measured values of 1.4 ms and 6768 cm^{-1}. The next-lowest-energy state ($a2$) is predicted to have a lifetime which is 80 times larger, a result which is consistent with the failure to date to observe emission bands initiating from this state.

1. Introduction

The low-lying states of the bismuth fluoride molecule have been the object of numerous spectroscopic studies [1–12]. The first observations of the BiF absorption and emission spectra in the 415–510 nm region were made by Howell [1] and Morgan [2] and date back to 1936. Rao and Rao [3,4] have analyzed the rotational structure of the emission spectrum in this range and assigned it to the $A0^+ – X_1 0^+$ transition. It was thoroughly reinvestigated by Jones and McLean [5], who confirmed this assignment. These authors also observed another feature [6], which was attributed to the $B0^+ – X_1 0^+$ transition and obtained spectroscopic constants for the $X_1 0^+$, $A0^+$ and $B0^+$

states [5], the first set of which agree well with the values for $X_1 0^+$ based on microwave data [7]. The same authors [6] concluded that another 0^+ state ($b0^+$ in their notation) exists at an energy of 9216 cm^{-1} above the $X_1 0^+$ ground state. From the analysis of the observed spectra an important conclusion [5] was made about perturbations of the $A0^+$ state due to the A–B coupling. Another state (perhaps two) was also inferred which perturbs the $B0^+$ rovibrational levels and possesses a T_0 value in the 26550–28300 cm^{-1} range. In addition, in ref. [8] the radiative lifetimes for $A0^+$ levels with $v' < 6$ have been determined. Finally, several investigators [9–12] have observed the so-called "red" systems in the 565–740 nm spectral range, but the assignment of the states involved was not quite certain.

In 1986, exactly 50 years after the first experimental spectroscopic results for the BiF molecule had been

reported, the first theoretical investigation of this system appeared [13]. The very fact of such a delay indicates the considerable difficulties which needed to be overcome in order to make it possible to carry out meaningful calculations on molecules containing atoms as heavy as bismuth ($Z=83$). Using the relativistic CI method with spin–orbit (SO) coupling taken into account, Balasubramanian calculated potential curves of four low-lying states of BiF and computed their spectroscopic constants. He obtained the SO splitting for the ground state $X_1 0^+$ and $X_2 1$ components and also calculated the relative energies of the $2(I)$ and $0^+(II)$ states, the latter one usually designated in experimental studies as $A0^+$. From the results of these calculations [13] it was concluded that there is no 0^+ state in the 9200 cm^{-1} region, contrary to what had been suggested in ref. [6].

More recent experimental studies [14,15] have confirmed the above theoretical predictions for the $X_2 1$ state. Fink et al. [14] have observed $X_2 1 \rightarrow X_1 0^+$ infrared emission and obtained $T_0 = 6752$ cm^{-1} for the upper state, in fairly good agreement with the 7280 cm^{-1} value calculated by Balasubramanian [13]. From a new interpretation of previous spectroscopic data [16], these authors [14] have also concluded that the $2(I)$ state lies 11555 cm^{-1} above $X_1 0^+$, somewhat lower than the calculated value of 14595 cm^{-1} [13]. Devore et al. [15] have studied the emission spectrum in the 565–740 nm region and assigned it to two different transitions which both terminate in the $X_2 1$ state. The first one was designated as the $A'1$–$X_2 1$ transition, while the second was suggested to originate from another upper state, denoted A″ and lying 22552 ± 545 cm^{-1} above $X_1 0^+$ and thus virtually isoergic with $A0^+$.

Nevertheless, there still remain open questions about the excitation energy and nature of the $A0^+$ state. The experimental interpretation of refs. [3,6] has identified the $A0^+$ state with a $\sigma^2 \pi^3 \pi^{*3}$ electronic configuration, i.e. a $\pi \rightarrow \pi^*$ excitation relative to the ground state. The corresponding T_0 value is found to be 22960 cm^{-1} in the same work. According to Balasubramanian [13], however, it lies considerably higher (25931 cm^{-1}) and originates from the same configuration as the ground state ($\sigma^2 \pi^4 \pi^{*2}$). We will argue in this study that neither of these configurations is dominant for the $A0^+$ state near its equilibrium bond distance, but rather the $\sigma^2 \pi^4 \pi^* \sigma^*$ configu-

ration corresponding to a $\pi^* \rightarrow \sigma^*$ excitation relative to the electronic ground state.

To clear up this point and also to provide additional information regarding the low-lying states of BiF, including their radiative lifetimes, which can be helpful in explaining other details of the spectroscopic data, new calculations have been undertaken which are based on the multireference configuration interaction technique and employ effective core potentials including spin–orbit coupling effects. In addition, attention will be directed to a series of questions formulated by Fink et al. [14] with regard to various spectroscopic properties of the BiF molecule.

2. Method of calculations

In the present study we have employed relativistic core potentials within the framework developed in refs. [17–19]. In this approach relativistic core potentials averaged with respect to spin are included at the SCF step, while corresponding differences used to represent the SO operator are brought into the treatment at the CI level. We have used relativistic potentials generated in refs. [20] and [21] for the Bi and F atoms respectively. The s and p electrons of both bismuth and fluorine have been included in the valence set of our calculations, i.e. of the two sets of Bi potentials given in ref. [20], that in which the 5d electrons are contained in the core has been employed in the present treatment. For the Bi atom we have employed the (3s, 3p) Gaussian basis set in uncontracted form which was optimized for use with the corresponding core potentials of ref. [20]. It was augmented in this work by a d orbital with an exponent of 2.00 a_0^{-2}. For the F atom the (4s, 4p) basis set of ref. [21] augmented by a d orbital with an exponent of 0.8 a_0^{-2} was employed.

At the CI step calculations are carried out using the normal MRD-CI scheme described elsewhere [22,23]. All calculations are done in formal C_{2v} symmetry, and some technical details are given in table 1. A configuration selection procedure is employed based on an energy-lowering threshold value of $T=2.0 \times 10^{-5}$ E_h. The accuracy of the reference set choice can be characterized by the $\sum_p c_p^2$ value [22] for coefficients appearing in the final CI eigenvectors. This quantity is larger than 0.90 for all roots and

Table 1
Technical details of the MRD-CI calculations [a]

C_{2v} symm.	N_{ref}/N_{root}	SAFTOT/SAFSEL	$C_{\infty v}$ notation	Σc_p^2
$^1A_1$	38/6	124100/2450	$^1\Delta$	0.9567
			$^1\Sigma^+$	0.9463
$^1B_{1,2}$	27/4	103773/2429	$1\,^1\Pi_{x,y}$	0.9456
			$2\,^1\Pi_{x,y}$	0.9272
$^1A_2$	23/6	100012/2827	$^1\Delta$	0.9560
			$^1\Sigma^-$	0.9428
$^3A_1$	26/6	194137/2763	$^3\Delta$	0.9329
			$^3\Sigma^+$	0.9332
$^3B_{1,2}$	27/6	178199/2818	$1\,^3\Pi_{x,y}$	0.9511
			$2\,^3\Pi_{x,y}$	0.9412
$^3A_2$	23/7	175510/3825	$^3\Delta$	0.9567
			$^3\Sigma^-$	0.9408

[a] The number of selected SAFs and the Σc_p^2 values are given for $r=4.2\ a_0$. SAFTOT designates the total number of generated, SAFSEL the number of selected SAFs. N_{ref} and N_{root} refer to the number of reference configurations and roots treated.

symmetries involved in the relativistic CI (including SO) treatment. Numbers of reference configurations and roots employed and $\Sigma_p c_p^2$ values obtained are given in table 1 together with the corresponding $C_{\infty v}$ notation of the states treated.

The relativistic CI procedure itself is simple in design. A Hamiltonian matrix is constructed for each irreducible representation of the C_{2v} double group. The basis functions in each case are $\lambda-s$ configuration-state functions (CSFs) of the MRD-CI calculations coupled with appropriate C_{2v} spin functions. Following the suggestion of Pitzer and Winter [24], these functions are multiplied with $i=\sqrt{-1}$ in certain cases in order to insure that only real spin–orbit matrix elements result. The orders of the relativistic CI secular equations are typically four times as large as their counterparts at the non-relativistic level of treatment. Rapid convergence is generally obtained through the use of $\lambda-s$ eigenfunctions as starting functions for the diagonalization procedure. The resulting solutions are then used to obtain electronic transition moment results by combining data obtained from runs with the non-relativistic program available for this purpose.

Fig. 1. Potential energy curves of seven low-lying $\lambda-s$ states of BiF calculated without spin–orbit interaction.

3. Results and discussion

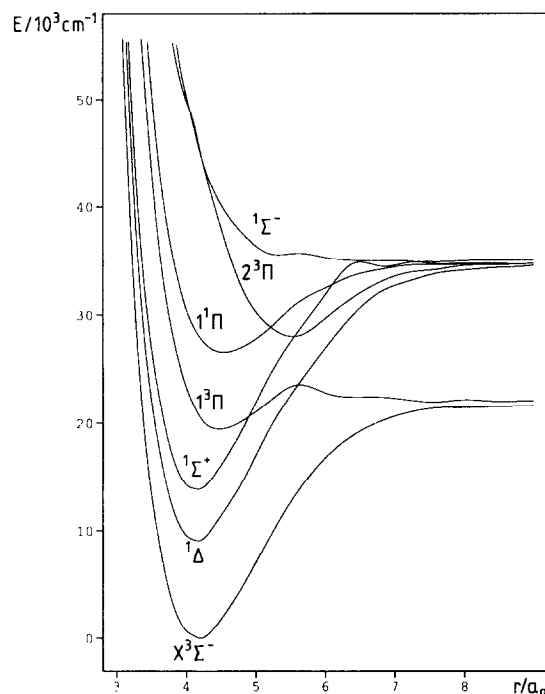The calculated MRD-CI potential curves for seven low-lying $\lambda-s$ states of BiF are shown in fig. 1. The main emphasis in the present study is to describe the electronic spectra of this system, and so attention has been restricted to those states which play a major role in the Franck–Condon region of the X_10^+ ground

state. Therefore some states of quintet multiplicity which correlate with the lowest asymptotes of the separated atoms have not been considered. Of particular interest in the present study is the location of the lowest $^3\Pi$ state. It correlates with the lowest $^4S_u + {}^2P_u$ asymptote, whereas the lowest $^1\Sigma^+$ state is forced by symmetry to merge with the $^2D_u + {}^2P_u$ atomic states.

The potential curves resulting from inclusion of the spin–orbit interaction are shown in fig. 2, while the spectroscopic constants of the corresponding states are given in table 2. These may be compared with various experimental results and also the theoretical estimates reported by Balasubramanian [13]. The lowest three states are found to be the $X_1 0^+$ and $X_2 1$ species, which result from the $^3\Sigma^-$ λ–s states (fig. 1), and the a2 $^1\Delta$ state which also derives from the same $\pi^4\pi^{*2}$ electron configuration. The zero-field splitting between the $X_2 1$ and $X_1 0^+$ states is computed to be 6937 cm^{-1}, in good agreement with the experimental value [14] of 6768 cm^{-1} and also with the previous theoretical value of 7280 cm^{-1} [13]. The corresponding T_0 value computed for the a2 state is 13930 cm^{-1}, which is nearly 2400 cm^{-1} higher than the ex-

perimental value inferred by Fink et al. [14] based on an interpretation of emission lines found in ref. [16]. The present value is 665 cm^{-1} lower than that found by Balasubramanian [13], and thus is in slightly better agreement with the above experimentally inferred result.

The equilibrium bond distance computed in the present treatment for the $X_1 0^+$ state is 0.186 Å greater than the measured value (table 2). Such a large discrepancy is attributable in the main to the choice of effective core potentials in the present treatment with all electrons of the Bi atom except those in the 6s and 6p shells included therein, and thus very similar effects are expected for the other electronic states under consideration. In section 4 we will examine this point in detail through the use of a different core potential [25] which does not include the effects of the 5d electrons. This second series of calculations verifies the above conclusion about uniform overestimations of equilibrium bond distances in the treatment to be discussed first, and thus suggests strongly that the corresponding potential curves are simply all translated by nearly the same amount relative to their exact counterparts. It therefore appears likely that the relationships computed between the various electronic states which are important in describing details of the intensity distribution in the various BiF transitions should still be quite reliable in analyzing the spectrum of this system.

The present relativistic CI treatment differs from the previous one [13] in a more significant way, however, namely in its description of electronic states of higher energy than a2. The most important distinction has to do with the number of low-lying 0^+ excited states reported in the two studies. We find two such states, with T_0 values differing by only 4400 cm^{-1}. There seems little doubt that these states should be assigned to the experimental $A0^+$ and $B0^+$ species [14], with T_0 values of 22956 and 26056 cm^{-1} respectively. The published work of Balasubramanian [13] only reports one such state, which is identified with the lower of the two observed states. In addition, two other states of 0^- and 1 symmetry respectively are computed in the present treatment to lie between the two 0^+ species. Comparison of figs. 1 and 2 shows clearly that the new states result primarily from the $^3\Pi$ λ–s electronic state which correlates with the lowest-energy asymptote of the separated at-
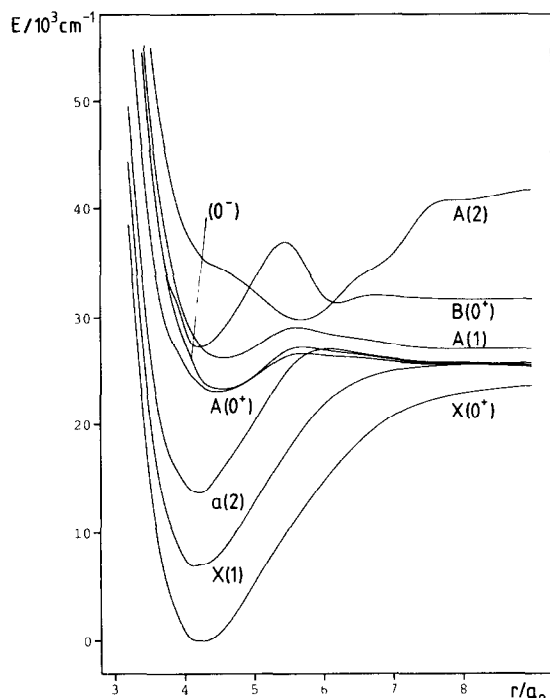

Fig. 2. Potential energy curves of eight low-lying states of BiF.

Table 2
Spectroscopic properties of BiF from various calculations and experiment (bond lengths r_e, transition energies T_0, vibrational frequencies ω_e and radiative lifetimes τ for $v'=0$)

State	r_e (Å)			T_0 (cm^{-1})			ω_e (cm^{-1})			τ (μs)	
	calc.		exp. [5]	calc.		exp. [14,28]	calc.		exp. [14,28]	calc. this work	exp. [28,30]
	[13]	this work		[13]	this work		[13]	this work			
X_10^+	2.087	2.238	2.052	0	0	0	502	476	508		
X_21	2.075	2.217		7280	6937	6768	501	503	538	1050	1400
a2	2.075	2.212		14600	13930	11555	511	481	527	80400	
$A_20^+(A)$	2.076	2.383	2.151	25913	23029	22956	467	342	383	1	2
$A_10^-(A'')$		2.414			23225	22544		355	412	95	50
$A_31(A')$		2.425			26155	24382		321	~400	6	16
B0$^+$		2.247	2.05		27405	26056		549	620	10	3

oms. On this basis the observed states with T_0 values of 22544 and 24382 cm^{-1}, denoted A″ and A′ respectively (table 2), can be assigned as the 0^- and 1 components of the unperturbed $^3\Pi$ λ–s state. The computed T_0 values for these two species are 23225 and 26155 cm^{-1}, in reasonably good agreement with the observed results.

The computed vibrational frequencies are also quite consistent with the above assignment (table 2). Especially interesting are the 0^+ values, which are computed to be 342 and 549 cm^{-1} for the A and B states respectively. The corresponding observed results of 383 and 620 cm^{-1} are both higher than the computed values, but they verify quite clearly that the lower of these two states has a significantly smaller vibrational frequency. The underestimation of these quantities in the theoretical treatment is consistent with its general tendency to predict equilibrium bond lengths which are too large compared to their experimental values. The discrepancies in the r_e values for A0$^+$ and B0$^+$ are 0.232 and 0.197 Å, which are similar to those noted above for the lower-lying X_10^+, X_21 and a2 states. The frequency underestimations are 41 and 71 cm^{-1} respectively for A0$^+$ and B0$^+$, which also fit in well with the errors noted for the same quantity for each of the three lower-lying states and also for the other two values in table 2 for the A″0$^-$ and A′1 states. The frequency computed in ref. [13] for its lone 0$^+$ excited state is 467 cm^{-1}, and thus lies in between the two observed results for the A and B states.

One can obtain more insight into the various cal-

culated results by analyzing the various CI expansions in each case, particularly for the three 0$^+$ states. To this end, the squares of these coefficients are listed in table 3 for a series of bond distances. These data make clear that the $^3\Pi$ contribution to the A0$^+$ state is quite small at distances well below the computed equilibrium value, but that it grows quickly as stretching occurs. At $r=4.0$ a_0 the contributions from the $^3\Sigma^-$, $^1\Sigma^+$ and $^3\Pi$ λ–s states are nearly equal. At still larger distances the $^3\Pi$ contribution dominates by far, whereas the second largest c^2 value comes not from the b $^1\Sigma^+$ λ–s state but from the $^3\Sigma^-$ of lower energy. These results stand in some contrast to what has been found in the earlier treatment of Balasubramanian [13], although his c^2 values are only reported for $r=4.0$ and 5.0 a_0. The largest c^2 value for the $^3\Pi$ λ–s states is only 18% (at the larger of these two r values).

The present results are somewhat surprising based on the potential curve results of fig. 1, which show the $^3\Pi$ λ–s state to lie higher than b $^1\Sigma^+$ by a significant margin until a bond distance of $r=5.0$ a_0 is reached. Near the computed ground state r_e value this energy difference is 6000 cm^{-1} for the unperturbed λ–s states, but in the same region the effects of spin-orbit coupling lower the 0$^+$ component of the $^3\Pi$ multiplet by 4000–5000 cm^{-1}, so that the impression based on fig. 1 alone is misleading. To this should be added the fact that the $^1\Sigma^+$ undergoes a strong spin–orbit interaction with X $^3\Sigma^-$ which therefore pushes this 0$^+$ state significantly higher in the spectrum than in the unperturbed case. These observa-

Table 3
Composition of the lowest 0^+, 1 and 2 states of BiF (c^2, %)

State	r (a_0)	$^3\Sigma^-$	$^1\Sigma^+$	1 $^3\Pi$	2 $^3\Pi$	$^1\Pi$	$^1\Delta$
X_10^+	3.5	74.6	20.9				
	3.8	71.7	21.6	5.0			
	4.0	69.1	20.2	9.0			
	4.6	65.5	19.1	13.1	0.3		
A_20^+ (A)	3.5	22.8	72.8				
	3.8	26.6	62.4	8.4	1.4		
	4.0	26.3	38.1	32.5	1.0		
	4.2	22.6	11.1	61.3	0.5		
	4.4	19.5	2.4	71.0			
	4.6	18.8		72.5			
$B0^+$	3.5		3.6	89.8			
	3.8		13.6	81.9	0.1		
	4.0	0.9	39.5	54.7	0.5		
	4.2	6.7	66.4	22.7	1.1		
	4.4	11.0	75.3	4.7			
	4.6	13.4	77.4	4.5			
X_21	3.8	97.3		1.1	0.3	0.6	
	4.2	95.9		1.9	0.3	1.1	
	4.6	94.3		2.7		1.5	
A_31 (A′)	3.8	0.3		75.9		23.1	
	4.2	0.4		73.3		25.5	
	4.6	0.6		72.6		25.3	
a2	3.8			3.7	0.7		94.0
	4.2			6.9	0.7		91.3
	4.6			11.1			86.8

tions emphasize that three 0^+ unperturbed states play a strong role in the interactions which lead to the observed A and B states. Some evidence of this phenomenon is already seen in the expansion of the X_10^+ ground state, in which the b $^1\Sigma^+$ makes a nearly constant 20% contribution at all bond distances. The $B0^+$ state is seen from table 2 to result almost exclusively from the $^3\Pi$–$^1\Sigma^+$ interaction. Even in this case, however, it is found that the third component ($^3\Sigma^-$) begins to make a significant contribution for values as large as $r=4.4$ a_0. As the upper adiabatic component of a sharply avoided curve crossing, the $B0^+$ state is characterized by an unusually large vibrational frequency, one that is greater (620 cm^{-1}) than one would expect on the basis of the unperturbed frequencies of any of its three major λ–s components.

These results answer in a quantitative manner the question raised by Fink et al. [14] regarding the fact that the frequencies of the $X0^+$ and $A0^+$ states are so different, despite the fact that the calculations of ref. [13] indicate that they both arise from the same ($\sigma^2\pi^4\pi^{*2}$) electronic configuration. The observed data are far easier to understand on the basis of the present treatment which indicate a heavy admixture of $^3\Pi$ character, with its longer r_e value and smaller vibrational frequency, to the $A0^+$ state. The present calculations also provide an explanation for the smaller effect observed for the frequencies of the X_21 and a2 states, namely that they are 20–30 cm^{-1} larger than for X_10^+. Again the admixture of the $^3\Pi$ λ–s state to these various Ω states seems to be responsible for these trends, with far smaller $^3\Pi$ c^2 values being found for the X_21 and a2 species in table 3 than for X_10^+.

There has been some controversy about the dissociation energy of the BiF molecule in its ground electronic state, with estimates for this quantity ranging from 2.5 to 5.0 eV. Devore et al. [15] have recently argued on the basis of chemiluminescent reactions

involving atomic and diatomic bismuth and fluorine systems that the BiF bond energy lies in the neighborhood of 5 eV. Gaydon [26] has estimated a value of 2.65 ± 0.2 eV, and Balasubramanian [13] has computed a result of 2.63 eV, in very good agreement with the latter result. Jones and McLean [5] also have given an estimate for this quantity based on an interpretation of the $A0^+$ vibrational level progressions which is consistent with the latter suggestions, finding it to be less than 3.14 eV. More recently Yoo et al. [27] have deduced a D_0 value of 3.76 ± 0.13 eV based on three independent sets of measurements. Our own calculations for a series of states which correlate with the ground state asymptote lead to a value of 3.1 ± 0.1 eV, and are therefore much more consistent with all previous estimates than with that of Devore et al. [15].

In order to further characterize the BiF electronic states electric dipole transition moments μ have been computed, and these results have been related to the lifetimes of the various excited states according to the formula for the Einstein coefficient (s^{-1}):

$$A = 2.026 \times 10^{-6} |\mu|^2 \Delta E^3 , \qquad (1)$$

where μ is given in units of ea_0 and ΔE is the corresponding transition energy in cm^{-1}. The lifetime τ is then obtained as

$$\tau = \left(\sum_i A_i \right)^{-1} , \qquad (2)$$

where the sum is over lower-state vibrational levels.

The $X_2 1$ state has a fairly long lifetime of slightly more than a millisecond according to these computations, which is in good agreement with the observed value of Fink et al. [28] of 1.4 ms (table 2). The non-zero dipole matrix element arises from the $^1\Sigma^+$ admixture in $X_1 0^+$, which in turn can interact with the weak $^1\Pi$ component of $X_2 1$ (table 3), as well as the $^3\Pi_0 - ^3\Sigma_1^-$ first-order contribution expected from the presence of a strong $^3\Pi$ component in $X_1 0^+$. By contrast, the a2 state is much less able to undergo spontaneous transitions to either of the two Ω states below it. The transition to $X_1 0^+$ is forbidden by the dipole selection rules, and the corresponding allowed transition to $X_2 1$ is extremely weak. Hence the a2 lifetime is computed to be 80 times larger than that of the $X_2 1$ state.

The first relatively strong transition in table 2 occurs between $A0^+$ and $X0^+$. Analysis of the computed results shows that the partial lifetime for the $v' = 0$ level of $A0^+$ is 0.972 μs, whereas the corresponding result for $A0^+ - X1$ is nearly 100 times longer (91.97 μs). The total lifetime of 1.0 μs is in good agreement with the measured value of 2 μs [28]. The relatively large μ_0 value for the parallel transition arises because of $^3\Pi - ^3\Pi$ and $^1\Sigma^+ - ^1\Sigma^+$ dipole matrix elements which receive large weighting because of the spin-orbit effects in the 0^+ states already discussed. The only real source of intensity for the perpendicular transition by contrast is the $^3\Pi - ^3\Sigma^-$ component, the magnitude of which decreases with increasing bond distance. The dominance of μ_0 over μ_1 for the $A0^+ - X$ transitions agrees with the experimental findings of Fink et al. [14], and the above analysis also makes clear why this is exceptional behavior [29] for group V diatomic halides in which the lighter of the two atoms is the halogen. Normally the $A0^+$ state, i.e. the lowest-lying excited 0^+ species, is composed almost exclusively of the b $^1\Sigma^+$ λ-s state. Transitions between b $^1\Sigma^+$ and the spin-perturbed $^3\Sigma^-$ ground state are notably weaker than those involving a $^3\Pi_{0^+}$ upper state. Once again anomalous behavior of the BiF molecule thus turns out to be explained in terms of the unusually high admixture of the $^3\Pi$ λ-s state in the lowest-lying 0^+ excited state of this molecule. It also is worthwhile to note that Jones and McLean [5,6] have observed a cutoff of bands above $v' = 5$ in the $A0^+ - X_1 0^+$ transition which involve the repulsive limbs of the associated potential curves. Such behavior might also be explained by the rapid changes in the constitution of the $A0^+$ state for these energies (or r values) from $^3\Pi_0$ to b $^1\Sigma^+$ (table 3). As a result, estimations of the $X_1 0^+$ D_0 value based on these phenomena are of doubtful validity, since they are not necessarily an indication of predissociation in the $A0^+$ state, contrary to what has been inferred in ref. [5].

The analysis of the lifetime results is complicated by the fact that the dipole matrix elements, which are the main input for these quantities, are found to vary strongly with internuclear distance, as can be seen from figs. 3a and 3b. It is found, for example, that the magnitude of the $A0^+ - X_1 0^+$ moment increases almost linearly with r_e (fig. 3a), while the corresponding $A0^+ - X_2 1$ quantity shows opposite behavior. Since
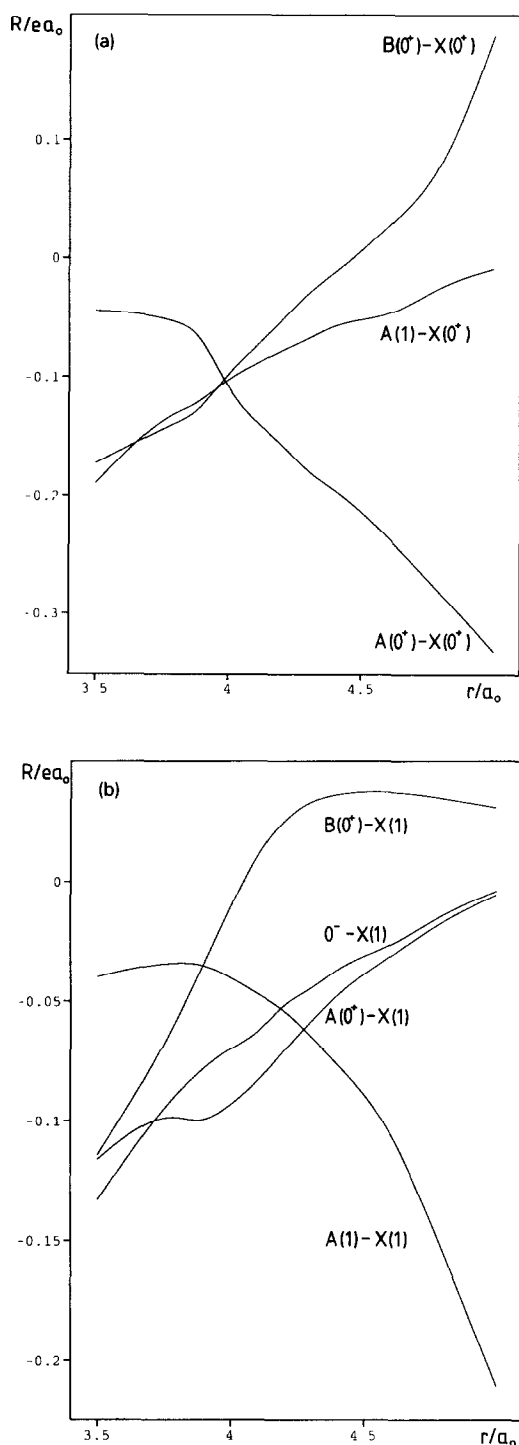
Fig. 3. Calculated transition dipole moment curves involving the $X_1 0^+$ (part a) and $X_2 1$ (part b) states.

lifetimes are computed for the upper state vibrational levels, the results for relatively large bond distances ($r \sim 4.5\ a_0$) tend to dominate in the corresponding computations, and this turns out to be the main reason why the parallel μ_0 component is so much larger than μ_1 in this case.

Similar results are also found for the B–X transition moments. In this case the partial lifetime for the parallel transition is 12.38 µs, while that for perpendicular transitions is 98.25 µs. The total lifetime is computed to be 10 µs ($v' = 0$), compared with a recent experimental value of 2.97 ± 0.06 µs [30]. In this case it might well be expected that the parallel transition would benefit more from the $^1\Sigma^+ - ^1\Sigma^+$ contributions expected from the c^2 data of table 2. Such a result is found, but it is balanced to a large extent by a $^3\Sigma^- - ^3\Sigma^-$ contribution of opposite sign. The $^3\Pi - ^3\Pi$ results are also fairly large ($0.25\ ea_0$ at $r = 4.3\ a_0$, for example), but the net result is a large cancellation effect at almost all bond distances (fig. 3a), with μ_0 vanishing near $r = 4.5\ a_0$ and μ_1 becoming zero near $r = 4.0\ a_0$. Observed perturbations of the $v' = 0–3$ levels of $B0^+$ are most probably caused by rotational coupling with the $A'1$ state, which is computed to lie in the immediate neighborhood according to the present calculations. This conclusion is also supported by the fact that the perturbations reported in ref. [5] occur for rather high rotational quantum numbers ($J' = 51–82$).

Results have also been obtained for the $0^- - X_2 1$ and $A'1 - X_1 0^+, X_2 1$ transitions. In the first case a lifetime of 95 µs is indicated, nearly 100 times weaker than for the $A0^+$ value. The experimental data of Fink et al. [28] indicate that the actual value is about half this long (50 µs), but this level of agreement should be taken as quite satisfactory considering the various uncertainties involved in the computations. The lifetime of the $A'1$ state is found to be 6 µs in the present treatment. In this case there is both a parallel and a perpendicular component, and the latter is found to be larger. The partial lifetime for the parallel component is 18.16 µs, while the other is 8.98 µs.

Before concluding this section a word about notation is in order. For lighter systems it has become standard [31] to label all Ω states deriving from the $^3\Pi$ λ–s species with A_i, $i = 1$, 4, i.e. in increasing energy order. We have attempted to maintain this convention for BiF even though it is clear that at least

the 0^+ member is actually a heavy mixture of several different λ–s states, especially $^1\Sigma^+$ and $^3\Sigma^-$. It is also clear that the practice of using capital letters for states of the same multiplicity as the ground state and small letters for all others is difficult to follow for systems in which a large amount of spin–orbit coupling is present. For this reason we have referred to the third 0^+ species as B, in agreement with experimentalists' usage. It also should be noted that the heavy mixing among pure λ–s states has an effect on the normal order of $^3\Pi\,\Omega$ states, as least in the present calculations. Since experiment indicates that 0^- has a T_0 value which is still 412 cm^{-1} lower than the nearest 0^+ species, we have thus labelled these states as $A_1 0^-$ and $A_2 0^+$ respectively even though the calculations show the reverse order. It is certainly conceivable that in some other case such mixing will be sufficient to upset the regular (or inverted order) of multiplets, which situation would then present an additional source of uncertainty in applying the Huber–Herzberg designation scheme [31].

4. Additional calculations with a different effective core potential

The main prerequisite in carrying out CI calculations on molecules containing such heavy atoms as bismuth is a reliable effective core potential (ECP) for the inner shells, since a conventional all-electron treatment is quite impractical. In the preceding discussion the calculations have been carried out with an ECP from ref. [20] which describes all the bismuth shells through 5d, i.e. only the 6s, 6p electrons are considered explicitly in the CI treatment itself. While these calculations have generally given a quantitatively satisfactory description of the key spectroscopic data of interest, it has been noted that they are subject to a relatively large error in the equilibrium bond lengths of the various BiF states (~ 0.2 Å). In section 3 it was argued that this effect is caused mainly by the choice of ECP in the theoretical treatment. In the present section this thesis is tested by means of additional calculations which employ a different bismuth ECP from ref. [25]. The main difference between this ECP and the one employed in the first part of this paper is the number of electrons described in the effective core, with the 5d electrons now being

included in the valence space. The SCF calculations are thus carried out with 22 electrons in occupied shells in the second treatment, as compared to only 12 in the first case. Nevertheless, the number of active electrons in the CI, i.e. which are distributed over the one-electron basis in a variable manner is the same (12) as in the first set of calculations (figs. 1–3 and tables 1–3). The same number of valence electrons were included in the respective SCF and CI treatments of ref. [13]. The same Bi s, p valence basis is employed as in the first treatment, but three d functions [20] in a [2,1,1] contraction are present in this case as opposed to the single primitive species employed in sections 2 and 3. The fluorine ECP [21] employed in the first set of calculations is maintained in the present treatment. The earlier study of Balasubramanian [13] by contrast describes the 1s electrons of this atom explicitly in the SCF and CI calculations, i.e. without the use of an ECP.

The results of the CI calculations with the second bismuth ECP [25] are summarized in table 4. A very positive effect is noted with regard to the computed equilibrium bond lengths. In the case of the $X_1 0^+$ ground state a decrease of 0.125 Å is found relative to the result with the first ECP (table 2). There is still an overestimation compared to experiment, but it is reduced to 0.061 Å. This error can be compared to that obtained in ref. [13], namely 0.035 Å. Hence a small portion of the original discrepancy between the two computed r_e values is caused by differences in CI treatment (including distinctions in the way the fluorine 1s electrons are described), but most of it simply results from the choice of bismuth ECP [20] in the first set of calculations in the present work.

The computed decrease in bond length in the sec-

Table 4
Spectroscopic properties of BiF computed with an ECP from ref. [25]. See table 2 for comparison with experimental and other theoretical results

State	r_e (Å)	T_0 (cm^{-1})	ω_e (cm^{-1})
$X_1 0^+$	2.1128	0	534
$X_2 1$	2.1020	7163	538
$a2$	2.0856	12218	561
$A_2 0^+ (A)$	2.2154	24311	342
$A_1 0^- (A'')$	2.2660	24450	484
$A_3 1 (A')$	2.2485	27348	468
$B 0^+$	2.1408	26817	636

ond treatment is a general trend observed for all electronic states. In the case of the $A0^+$ state the decrease is somewhat larger (0.168 Å), whereas for $B0^+$ it is only 0.106 Å. For the A_10^- and A_31 states the computed decreases lie in the 0.15–0.17 Å range, similarly as for $A0^+$. Thus as stated in section 3, the indication is that the relationships between the various potential curves of the low-lying BiF electronic states are not greatly affected by improvements in the theoretical treatment relative to the original calculations.

The T_0 values obtained with the new bismuth ECP [25] are in generally good agreement with those of table 2. The result for X_21 is 226 cm^{-1} larger, while that for a2 is 1712 cm^{-1} smaller. In the first case the error compared to experiment is thus increased to 395 cm^{-1}, while in the latter it is reduced to 663 cm^{-1}. For the four highest states in the two tables, higher T_0 values are computed in each case. For $A0^+$ the increase is 1355 cm^{-1}, whereas for $B0^+$ it is 761 cm^{-1}. Balasubramanian [13] reports a single energy result for $A0^+$ of 25931 cm^{-1}, which is in better agreement with the present T_0 value for $B0^+$. Comparison of the c^2 contributions for λ–s states in the new treatment with those of table 3 shows that relatively little change has occurred in this respect. This is especially true for the X_10^+ ground state, which continues to have a roughly 20% contribution from the $^1\Sigma^+$ λ–s state at all distances in the neighborhood of the equilibrium value. The point of the avoided crossing between $A0^+$ and $B0^+$ is shifted to $r=4.0\ a_0$ in the second treatment, which is close to the computed ground state equilibrium distance in that case. In table 3 the equivalent point is reached at nearly the same r value, although in this case this corresponds to a bond distance which is 0.15 a_0 smaller than the X_10^+ equilibrium value obtained in this treatment. There thus seems to be a clear distinction between the present calculations and those reported in ref. [13] in this important aspect. It is worth noting that only a limited set of excitations relative to the $^3\Pi$ were considered in ref. [13], and this restriction may be a root cause for the above deficiency. It is therefore of great interest to carry out calculations for both low-lying 0^+ excited states employing the treatment of ref. [13] in order to shed further light on the origin of this distinction.

As expected, the general decrease in equilibrium bond lengths obtained through the use of a different

bismuth ECP [25] is accompanied by a corresponding increase in the vibrational frequencies of the various BiF states treated. In some cases the new frequencies (table 4) now exceed their observed values, despite the fact that all the computed bond lengths are still too large. The only exception to the pattern of overestimation is the $A0^+$ result, which remains at 342 cm^{-1} in the second treatment, 41 cm^{-1} less than the observed value. The result for X_21 is equal to the measured frequency, while the data for X_10^+, a2 and $B0^+$ exceed their observed values by roughly 30 cm^{-1}. The overestimations for the A_10^- and A_31 frequencies are larger (60–70 cm^{-1}). The relatively poor result for A_31 is perhaps related to the fact that the T_0 value for this state shows the greatest error (≈ 3000 cm^{-1}) relative to experiment as well.

Finally, a series of tests carried out in the $r=3.8$–4.8 a_0 region indicate that the transition moment results are relatively independent of which of the two ECPs is employed in the CI calculations. Thus the results given in table 2 still constitute the best estimates for the experimental lifetimes obtained in the present study.

5. Conclusion

A CI treatment of the low-lying BiF electronic states has been carried out with the aid of relativistic effective core potentials (ECPs), including spin–orbit coupling effects. The main conclusion of this work is that Ω states with a heavy contribution from the $^3\Pi$ λ–s state are quite important in understanding the spectrum of this molecule in the T_0 range of 22000–26000 cm^{-1}. It is found, for example, that the lowest 0^+ excited state contains more $^3\Pi$ than b $^1\Sigma^+$ character, especially at bond distances greater than the equilibrium value for X_10^+, and this fact produces a number of interesting effects in the BiF spectrum. It causes the r_e value of $A0^+$ to be 0.10 Å larger than that of X_10^+, for example, and gives it a vibrational frequency which is 125 cm^{-1} smaller as well. An avoided crossing between the $^3\Pi$ and b $^1\Sigma^+$ λ–s states also leads to an upper state with a relatively high vibrational frequency (620 cm^{-1}). In addition the $^3\Pi$ contribution to $A0^+$ causes its radiative lifetime to be relatively short and to make the parallel component (to X_10^+) of its transition moment to the λ–s

ground state to be much larger in magnitude than the corresponding value for the perpendicular transition. There is also an indication that the perturbations of the 0^+ states continue to higher energies in the BiF spectrum, and this circumstance may provide the basis for answering a question posed by Fink et al. [14] regarding the absence of a $^3\Pi_0-X_2 1$ subsystem in emission to accompany the observed $^3\Pi_2-X_2 1$ activity.

The present calculations find the a2 state which results from the $\pi^4\pi^{*2}$ electronic configuration to lie in the 12200–13900 cm^{-1} range, which also lends support to an interpretation of Fink et al. [14] based on earlier experimental data [16] which attributes a T_0 value of 11555 cm^{-1} to this state. The present computed zero-field splitting for the $X_1 0^+-X_2 1$ states of 6836 cm^{-1} is also in good agreement with the measured value of 6768 cm^{-1}. In addition, two other recently observed states (A″ and A′) are given definite assignments of $\Omega=0^-$ and 1 respectively on the basis of the present calculations. They are also found to be dominated by the $^3\Pi$ $\lambda-s$ state.

Radiative lifetimes have been computed for six excited states of the BiF molecule, five of which have been determined experimentally. The calculated values generally agree with the observed results within a factor of two to three, with $A0^+$ having the shortest lifetime of this group of states (2 μs [28]). The $A_1 0^-$ state is computed to have a radiative lifetime of 95 μs, whereas the corresponding measured value (A″) is 50 μs [28]. A recent experimental value for the lifetime of the $B0^+$ state is only 30% of the present computed result, so the error limits of the calculations appear to be somewhat greater in this instance. The spin-forbidden $X_2 1-X_1 0^+$ emission process causes the upper states to have a lifetime of 1.4 ms [28], nearly 1000 times larger than for $A0^+$, while the calculations give a value of 1.05 ms. The lifetime of the a2 state has not been measured as yet, but is predicted in the present work to be 80 times larger than that of $X_2 1$.

The computed equilibrium bond lengths are found to be quite dependent on the choice of ECP, but the effect is uniform for all electronic states, so that such deficiencies in the theoretical treatment do not greatly affect the key relationships between upper and lower states which determine the nature of the molecular spectra of such heavy-atom systems. Tests with two

different ECPs which differ in whether the 5d electrons are included or not show that better results for the equilibrium bond lengths of the BiF states are obtained when the 6s, 6p and 5d electrons are included in the valence space for the calculations. The results for the lifetimes and transition energies are less sensitive to such details of the theoretical treatment, although a general tendency toward higher T_0 values for the excited states with significant $^3\Pi$ $\lambda-s$ character is noted when the ECP without 5d electrons is employed.

In summary the present CI treatment including spin–orbit effects gives a reliable description of the details of the BiF electronic spectrum up to excitation energies of 30000 cm^{-1}. There is thus reason for optimism that similar treatments employing the same or analogous ECPs for molecules containing quite heavy atoms will be able to produce excitation energy and transition probability results which can be very useful in arriving at the correct interpretation of the corresponding observed spectroscopic data.

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