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Spin-orbit configuration interaction study of the potential energy curves and radiative lifetimes of the low-lying states of bismuth hydride

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An *ab initio* configuration interaction (CI) study including the spin-orbit coupling interaction is carried out for the lowest 23 states of the bismuth hydride molecule by employing relativistic effective core potentials for the bismuth atom. The computed spectroscopic constants are in good agreement with corresponding experimental data, although there is a tendency to overestimate bond lengths by 0.05–0.10 Å and to underestimate the vibrational frequencies accordingly. The BO^+ excited state is found to have no dissociation barrier, and its radiative lifetime is computed to be 4.3 μ s, with parallel transitions to X_10^+ being significantly stronger than the perpendicular $B-X_21$ species. The experimental EO^+ state is assigned as the third root of this symmetry and its potential curve possesses a dissociation barrier of 1840 cm^{-1} . This result explains the predissociation characteristics observed for this state and is also consistent with the failure to observe emission from it when attempts are made to form it in recombination processes. This barrier also needs to be taken into account in estimating the X_10^+ dissociation energy of this molecule from existing experimental data, and on this basis a D_e value of 2.28 eV is obtained which is in reasonably good agreement with the present directly computed result of 1.98 ± 0.06 eV. A number of other bound states and avoided crossings are indicated in the calculations which may be of relevance in future experimental investigations of this system.

I. INTRODUCTION

The first spectroscopic investigations of the bismuth hydride molecule were carried out in the early 1930s by Heimer and Hulten.¹ They observed three emission systems with 0–0 bands at 4698, 6118, and 4842 Å which were assigned to the $B^1\Sigma-X^1\Sigma$, $B^1\Sigma-A^1\Pi$, and $B^1\Sigma-C^1\Sigma$ transitions, respectively. These authors also reported the first observation of hyperfine structure (hfs) in the optical spectra of molecules based on their work with the $B-A$ transition. Later Heimer² carried out a more detailed study of these emission bands, and Hulten and Neuhaus³ and Neuhaus⁴ performed an hfs analysis of the $B-A$ spectrum. It should be noted that Heimer and Hulten^{1,2} also reported a $B^1\Sigma-C^1\Sigma$ transition lying at 4842 Å which apparently has not been confirmed in more recent experiments. A fourth BiH band system was found in absorption by Khan and Khan,⁵ which they attributed to the $E^1\Sigma-X^1\Sigma$ transition. It was later remeasured by Lindgren and Nilsson,⁶ who determined spectroscopic constants for the ground and upper states which are in good agreement with those found originally.⁵ These authors also observed the disappearance of rotational lines beginning with the $v'=2$ level of the EO^+ state, which they explained in terms of a strong predissociation caused by some repulsive state converging to $\text{Bi}(^2D_{3/2}) + \text{H}(^2S_{1/2})$. In spite of considerable efforts in this study, they were unable to observe emission from the EO^+ state. They concluded that some weaker type of predissociation must also be involved which affects the entire electronic state. Recently Fink *et al.*⁷ have carried out a

thorough investigation of the $A1-X0^+$ emission band near 2.02 μ m with the aid of a Fourier transform spectrometer, determining molecular constants for both the upper and lower states. Finally, the infrared rovibrational spectra of BiH and BiD have been studied within the last few years by means of diode laser spectroscopy^{8,9} and Fourier transform spectroscopy.¹⁰ On this basis accurate Dunham coefficients for the ground $X0^+$ state of BiH have been determined.

The first theoretical study of this system was reported by Balasubramanian,^{11,12} who carried out *ab initio* calculations of ten low-lying electronic states employing relativistic effective core potentials (RECPs) and a spin-orbit configuration method developed by Pitzer *et al.*^{13–16} The RECP for the bismuth atom chosen for this study was that given by Christiansen.¹⁷ With the aid of these calculations^{11,12} it was shown that numerous avoided crossings occur in the low-energy spectrum of this molecule, causing a fairly complicated appearance for its potential curves. The EO^+ state found by Khan and Khan⁵ in absorption was assigned by Balasubramanian¹² as the fourth 0^+ root calculated in his study based on the corresponding computed bond length (r_e) and vibrational frequency (ω_e) values. Nevertheless, rather large discrepancies were noted between theory and experiment for both r_e (0.33 Å) and the EO^+-X0^+ excitation energy ($\sim 5800 \text{ cm}^{-1}$), thus leaving open some questions regarding the correctness of this assignment. Several more recent theoretical studies^{18–20} have provided additional computed estimates of the ground-state bond distances, as well as of its dissociation energy and electric dipole moment.

Similar relativistic CI calculations have recently been carried out with a program system developed in our labo-

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ratory, for the bismuth fluoride system.²¹ One of the most surprising results of this study was the computation of relatively large equilibrium bond lengths for both the ground and excited states when the full-core RECP of Ross *et al.*²² was employed. Better agreement with experiment was found for BiF when the same Christiansen RECP¹⁷ was employed as in the Balasubramanian BiH study discussed first.^{11,12} Nevertheless, radiative lifetimes computed on the basis of the full-core ECP²² were found to be in satisfactory agreement with corresponding experimental results. The analogous results obtained with the RECP of Ref. 17 are generally quite similar. Computed transition energies resulting from both of these theoretical treatments also agree well with experiment. In view of the open questions about the interpretation of the experimental data for the BiH molecule discussed above and also the fact that radiative transition probabilities have yet to be computed in earlier theoretical work on this system, it seemed of interest to carry out new calculations for this molecule employing the same method as in the BiF study.²¹ Of special interest in this regard is the question of whether the rather poor bond length results obtained with the full-core ECP of Ref. 22 for the BiF molecule are carried over to BiH, especially since the type of bonding in the two systems is quite different.

II. COMPUTATIONAL DETAILS

In the present work we have employed relativistic core potentials within the framework developed in Refs. 13–16. In this approach relativistic potentials averaged with respect to spin are included at the self-consistent field (SCF) level of treatment, while corresponding differences of these potentials employed to represent the spin–orbit interaction are brought into play at the configuration interaction (CI) stage. In the present work the full-core RECP for the bismuth atom given by Ross *et al.*²² has been employed. All electrons other than those in the 6s,6p shells are thus incorporated in the core, both at the self-consistent field (SCF) and CI levels of treatment. The (3s,3p) Gaussian basis recommended²² for use with this RECP is employed in uncontracted form, along with an additional *d* orbital with an optimized exponent of 0.22 a_0^{-2} . The corresponding basis for the hydrogen atom is the 5s primitive set of Dunning,²³ contracted to 3s and augmented by a single *p* function with exponent 1.0 a_0^{-2} .

The configuration interaction calculations are carried out with the conventional multireference single- and double-excitation (MRD-CI) method,²⁴ including configuration selection and energy extrapolation. The Table CI algorithm and the corresponding computer program system²⁵ are employed to obtain the energies and one-electron properties of the λ -s electronic states prior to the inclusion of spin–orbit coupling effects. The generalized Davidson correction^{26,27} is also applied to the MRD-CI results in the usual manner. The SCF MOs of the $X^3\Sigma^-$ ground state with a $\sigma^2\pi^2$ electronic configuration are employed at each internuclear distance to construct the orthonormal sets of single-determinantal many-electron functions needed for the MRD-CI treatment. The calculations are carried out in

TABLE I. Technical details of the MRD-CI calculations.^a

C_{2v} symmetry	$N_{\text{ref}}/N_{\text{root}}$	SAFTOT/SAFSEL	$C_{\infty v}$ notation	Σ_p^2
1A_1	63/6	24 734/1989	$1^1\Delta$ $1^1\Sigma^+$	0.9598 0.9603
$^1B_{1,2}$	44/3	21 534/1586	$1^1\Pi_{x,y}$ $2^1\Pi_{x,y}$	0.9584 0.9654
1A_2	32/3	17 297/1341	$1^1\Delta$ $1^1\Sigma^-$	0.9687 0.9538
3A_1	42/3	30 187/2026	$1^3\Delta$ $1^3\Sigma^+$	0.9449 0.9521
$^3B_{1,2}$	44/3	33 968/1937	$1^3\Pi_{x,y}$ $2^3\Pi_{x,y}$	0.9576 0.9658
3A_2	30/4	26 906/1728	$1^3\Sigma^-$ $1^3\Delta$	0.9657 0.9561
5A_2	27/2	17 559/1111	$1^5\Sigma^-$	0.9637

^aThe number of selected SAFs and the Σ_p^2 values (for the lowest roots of each symmetry) are given for $r=3.5 a_0$. 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, respectively.

formal C_{2v} symmetry in order to take advantage of the simplicity of direct product relationships for irreducible representations of Abelian groups. Some technical details regarding numbers of reference configurations and roots computed for each λ -s symmetry type are given in Table I. A threshold value of $T=5.0 \mu E_h$ is employed for the selection of configurations and since there are only six active electrons in the CI, the error in the energy extrapolation procedure is only on the order of a few tenths of a millihartree in each case. The numbers of generated and selected configurations per λ -s symmetry type are also given in Table I. The correlation between C_{2v} and full (linear) point group representations is also shown in this table, as is the sum of squared coefficients Σ_p^2 for the reference configurations of the lowest roots computed. The latter values consistently fall between 0.95 and 0.97, which is a good indication that the reference sets have been judiciously chosen in each case. Previous benchmark tests²⁸ have indicated that the final Davidson corrected energies should be accurate to within 350 cm^{-1} (1.0 kcal/mol) of the corresponding exact full CI energies for the same atomic orbital (AO) basis.

The next step in the calculations involves the inclusion of spin–orbit effects at the CI level of treatment. For this purpose the various selected spatial configurations are multiplied with spin functions which transform according to irreducible representations of the C_{2v} double group and the resulting products are grouped together according to symmetry. Spin–orbit matrix elements are then computed between different configuration-state functions (CSFs) and these results are combined with the previous results for the spin-independent operator to form a Hamiltonian matrix representation for each of the four C_{2v} double group representations. The resulting secular equation orders are typically four to six times larger than for the original λ -s CI treatments (Table I), but the corresponding diagonalizations can be done in relatively few iterations in the Davidson procedure²⁹ because of the availability of excellent starting vectors from the spin-independent calculations.

The resulting energies are used directly without the addition of perturbative corrections analogous to those employed for the λ -s CI treatment. Because of the small numbers of active electrons, this procedure does not significantly detract from the overall accuracy of the computations in the present case. For larger numbers of electrons it proves advantageous to employ the λ -s eigenfunctions directly as basis functions for a rather small CI treatment, in which case the various standard perturbative corrections can be applied to the spin-independent Hamiltonian matrix elements. In the present case explicit tests have shown that both methods produce essentially the same results, both for total energies and various one-electron properties.

The resulting potential curves are fitted to polynomials and inserted in nuclear motion Schrödinger equations which are solved by means of the Numerov-Cooley method^{30,31} to obtain the desired vibrational wave functions and energies. In addition electric dipole moment expectation values are computed between different Ω states by summing up results obtained for their respective λ -s component functions which contain identical spin factors. These results are also fitted to polynomials and combined with the various vibrational functions obtained above in order to compute transition moments as a function of various pairs of vibrational quantum numbers in a given electronic transition. The resulting vibrational transition moments $\mu_{v'v''}$ (in ea_0) are then inserted in the formula for Einstein transition probabilities $A_{v'v''}$ in units of s^{-1} :

$$A_{v'v''} = 2.026 \times 10^{-6} |\mu_{v'v''}|^2 \bar{\Delta E}_{v'v''}^3 \quad (1)$$

where $\bar{\Delta E}_{v'v''}$ is the corresponding transition energy in units of cm^{-1} . The lifetime of a given vibrational state is then obtained in the usual manner by summing over the $A_{v'v''}$ values for all lower-lying vibrational states and inverting.

III. ENERGY RESULTS AND DISCUSSION

A. Calculated λ -s potential curves

The potential curves for the lowest 14 electronic states of bismuth hydride computed at the MRD-CI level with spin-independent averaged RECPs are given in Fig. 1. The corresponding set of adiabatic states spans the full set of asymptotes for the $4S_u$, $2D_u$, and $2P_u$ states of the bismuth atom in combination with the hydrogenic ground state. At short bond distances the most stable electronic configuration is the $\sigma^2\pi^2$ species, producing the familiar series of three multiplets: $X^3\Sigma^- < a^1\Delta < b^1\Sigma^+$. Of them the $X^3\Sigma^-$ state correlates with the $4S_u$ atomic ground state, while the $a^1\Delta$ and $b^1\Sigma^+$ converge to the $2D_u$ and $2P_u$ states, respectively. The only other diatomic state which correlates with $4S_u$ is the $5\Sigma^-$ of $\sigma\pi^2\sigma^*$ electronic configuration. It possesses a repulsive potential curve, which is an indication of the strengths of the bonding and antibonding characteristics of the σ and σ^* MOs, respectively.

The next most stable states are two pairs of $3,1\Pi$ species, originating from the $\sigma\pi^3$ and $\sigma^2\pi\sigma^*$ configurations. Their potential curves vary from slightly bonding to repul-

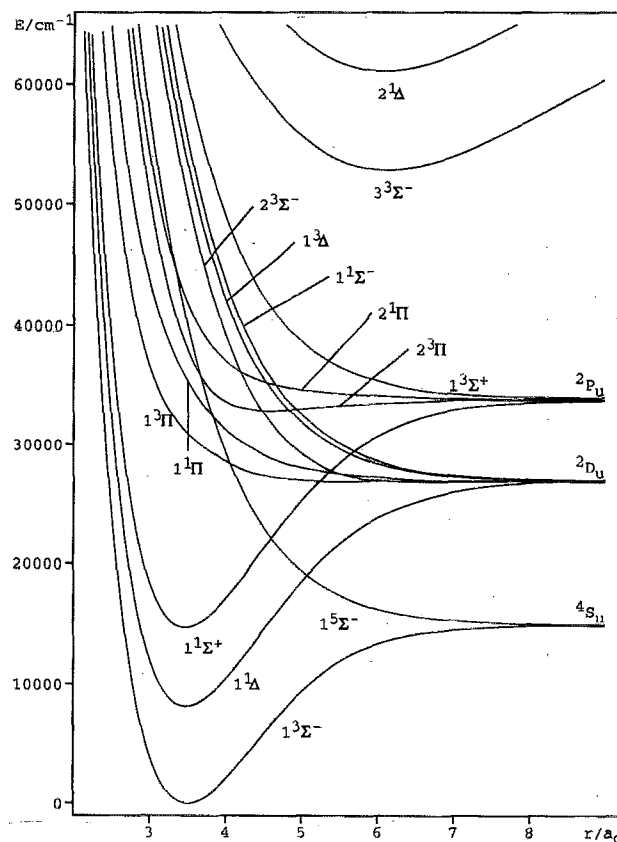


FIG. 1. Computed potential energy curves of the lowest-lying λ -s states of the bismuth hydride system obtained in a theoretical treatment without the inclusion of the spin-orbit interaction. The atomic dissociation limits correspond to $H(^2S_g) + Bi$ (as indicated).

sive in character (Fig. 1). In the former case this indicates that the π MO is considerably less bonding than the σ , which conclusion is consistent with the AO composition of these two orbitals. The other states in the diagram all stem from the same configuration as $5\Sigma^-$ and their potential curves are seen to become less repulsive with degree of excitation. Altogether eight λ -s states originate from the $\sigma\pi^2\sigma^*$ configuration, and of these only the $1^1\Sigma^+$ species is not shown in Fig. 1. The $3^3\Sigma^-$ and $2^1\Delta$ states of this group are found to possess potential minima near $r=6.0 a_0$, but are otherwise uninteresting for the description of the low-energy portion of the BiH spectrum as yet investigated experimentally. The first ionization potential of BiH has also been computed in the present study. A value of $67\,100\,cm^{-1}$ is obtained, which is in good agreement with an earlier theoretical result of $69\,053\,cm^{-1}$.¹⁹ It therefore appears unlikely that Rydberg states play a dominant role in the low-energy region of the BiH spectrum of primary interest in the present work.

B. Spin-orbit CI results

After the introduction of spin-orbit coupling the λ -s states discussed above split into their various components with a definite Ω quantum number. In this work a total of 23 such states will be considered, five of 0^+ , four of 0^- ,

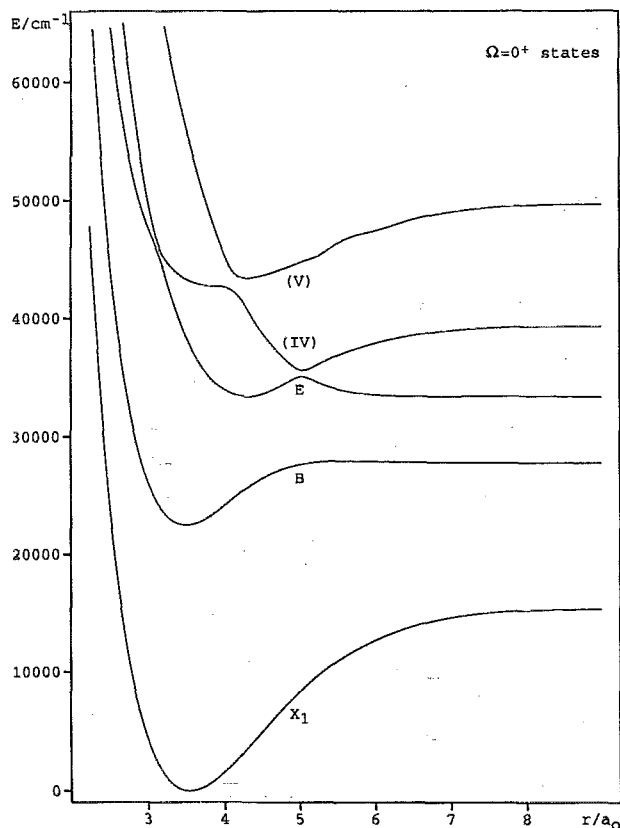


FIG. 2. Computed potential energy curves for the five lowest $\Omega=0^+$ states of the bismuth hydride molecule.

eight of 1, five of 2, and one of 3 symmetry. This represents an increase in the number of such states treated relative to the earlier theoretical study of Balasubramanian,¹² in which only ten such species are computed, four of 0^+ , one of 0^- , two each of 1 and 2 and one of 3 symmetry. Because of the importance of various avoided crossings in understanding the basic features of the BiH spectral data, we will first discuss the states of different Ω type separately.

1. The 0^+ manifold

The computed potential curves for the lowest five 0^+ states of bismuth hydride are given in Fig. 2. By far the most experimental information as yet gathered for this system pertains to states of this symmetry. There are a number of avoided crossings, the details of which can best be understood with reference to the CI expansion coefficients of various key electronic configurations in the corresponding states (Table II). There are five major terms of λ -s type which make major contributions to this group of states, namely $X^3\Sigma^-$ and $b^1\Sigma^+$ with a $\sigma^2\pi^2$ configuration, the first two $^3\Pi$ states, of $\sigma\pi^3$ and $\sigma^2\pi\sigma^*$ occupation, respectively, and finally the $2^3\Sigma^-$ species which derives from the same $\sigma\pi^2\sigma^*$ configuration as the repulsive $^5\Sigma^-$ λ -s state (Fig. 1). The $X_1 0^+$ ground state is a fairly constant mixture of 80% $X^3\Sigma^-$ and 20% $b^1\Sigma^+$ (Table II), except for large r values, for which the $\sigma^2\pi\sigma^*$ $^3\Pi$ state takes on increasing importance. The present computed spectro-

TABLE II. Composition of the lowest five 0^+ states of BiH (c^2 , %) at various bond distances r (in a_0). The leading configuration for each λ -s state is also shown.

State	r	$1^3\Sigma^-$ $\sigma^2\pi^2$	$1^1\Sigma^+$ $\sigma^2\pi^2$	$1^3\Pi$ $\sigma\pi^3$	$2^3\Pi$ $\sigma^2\pi\sigma^*$	$2^3\Sigma^-$ $\sigma\pi^2\sigma^*$
$X_1 0^+$	2.50	79.7	18.1	0.5	0.1	...
	3.50	77.4	18.6	...	2.3	...
	4.00	75.4	18.5	0.7	3.7	...
$B 0^+$	2.50	14.4	70.8	13.2	0.1	...
	3.50	17.6	68.8	11.8	0.4	...
	4.00	19.0	58.5	20.8	0.1	0.2
	4.25	19.6	48.2	29.8	0.1	0.6
	4.60	19.8	30.9	44.3	0.8	2.1
$E 0^+$	3.00	3.3	7.4	85.6
	3.25	...	4.4	12.6	79.3	...
	3.50	0.2	5.2	10.3	80.5	...
	4.00	0.1	13.8	26.9	55.1	0.1
	4.50	0.1	32.5	21.2	42.4	...
	5.00	0.4	32.8	14.9	30.3	18.8
$0^+ (IV)$	5.25	...	1.1	17.1	0.5	79.9
	2.50	...	0.3	...	94.7	0.6
	3.50	3.7	5.8	75.1	12.8	...
	4.00	4.1	7.0	48.1	34.6	4.4
	4.50	0.1	...	5.5	1.7	91.4
	5.00	0.1	11.1	2.2	15.3	69.2
$0^+ (V)$	5.25	0.5	42.8	1.1	47.9	3.7
	3.50	98.6
	4.00	0.3	0.8	1.1	2.5	94.0
	4.50	5.9	12.3	27.8	46.8	5.6
	6.00	8.8	34.3	17.3	30.8	6.9

scopic constants for this state are compared in Table III with available experimental and previous theoretical values for these quantities. The calculated r_e value is 1.867 Å, which is 0.062 Å larger than that found experimentally. Other theoretical results in the literature are 1.847 and 1.858,¹⁸ 1.869,¹⁹ and 1.90 Å,¹² so there has been a general tendency to overestimate this bond length. It should be recalled that a similar theoretical treatment with the same full-core bismuth RECP²² for the BiF molecule²¹ overestimated the ground-state r_e value for this system by 0.18 Å, however, a discrepancy which is almost three times larger than in the present BiH computations. This is at least an indication that the ionic bonding characteristics of the fluorine compound are far less accurately described with this type of RECP than is the nearly covalent bond in the present case of bismuth hydride.

The $X_1 0^+$ ω_e value is 1699.5 cm^{-1} , as determined by Heimer in 1935² and by Urban *et al.*⁹ and Heddrich and Bunath¹⁰ in more recent times. The corresponding $\Delta G(1/2)$ value is 1635.7 cm^{-1} .^{6,32} The present calculated ω_e value of 1632 cm^{-1} (Table III) is seen to underestimate the experimental result by 67 cm^{-1} . The ground state dissociates to the 4S_u bismuth atom asymptote and the value of the corresponding dissociation energy has also been a subject of some controversy. We will reserve discussion of this point until the results for the $E 0^+$ excited state are considered.

The second excited state of this symmetry is the $B 0^+$. The results of Table II show that its main component near $r=3.50 a_0$ is the $b^1\Sigma^+$ λ -s state, but major contributions

TABLE III. Spectroscopic properties of BiH from various calculations and experiment (bond lengths r_e , transition energies T_e , and vibrational frequencies ω_e).

State	r_e (Å)		T_e (cm ⁻¹)				ω_e (cm ⁻¹)		
	Calc.		Expt. ^a		Calc.		Calc.		Expt. ^a
	Other ^b	This work			Other ^b	This work	Other ^b	This work	
$X_1 0^+$	1.90 1.847 ^c 1.858 ^c 1.869 ^f	1.867	1.805 1.808 67 ^d		0	0	0	1619 1780 ^e 1756 ^e	1632 1699.5 ^g
$X_2 1$	1.89 1.840 ^e	1.854	1.791	5 737	4 303	4 917	1630	1618	1669 ^e
a_2	1.89	1.855	...	13 469	11 906	...	1630	1719	...
$B 0^+$	1.88	1.851	1.779 5	26 286	22 496	21 263	1585	1620	1643 ^e
$E 0^+$	2.51	2.283	2.177 2	38 780	33 364	32 940	1000	1215	1106 ^e
$0^+(IV)$...	2.669	35 575	2169	...
$0^+(V)$...	2.271	43 395	1528	...
$2 (II)$	2.58	2.521	...	23 450	24 100	...	1529	1013	...
$1 (III)$...	2.823	26 735	559	...

^aReference 32 unless otherwise indicated.^bReference 12 unless otherwise indicated.^cValue quoted is $\Delta G(1/2)$.^dReference 8.^eReference 18.^fReference 19.^gReferences 2, 9, and 10.

are also noted from the $X^3\Sigma^-$ and $\sigma\pi^3\Pi$ species. At larger bond distances the $^3\Pi \lambda$ -s component becomes gradually more important at the expense of $b^1\Sigma^+$. Near the dissociation limit the $2^3\Sigma^-$ also makes a strong contribution. The corresponding potential converges to the $^2D_{3/2}$ asymptote without a barrier. The latter feature is in some contrast to the results of Ref. 12, which indicate a fairly significant barrier to be present, with potential maximum in the neighborhood of $r=5.0 a_0$. At $r=3.5 a_0$ in this treatment only a rather small $\sigma\pi^3\Pi$ contribution of 8% is reported and no larger value is found as the bond distance is increased. Similar experience has been noted for the BiF molecule, for which the present spin-orbit CI method gives a relatively large $\pi\sigma^*^3\Pi$ contribution near the equilibrium bond distance of the lowest 0^+ excited state compared to the analogous calculations in the Balasubramanian study of the same system.³³ He also finds a far larger contribution from the $2^3\Sigma^- \lambda$ -s state at large r values for the $b0^+$ state of BiH (67% at $r=9.0 a_0$)¹² than is the case in the present work (Table II).

The absence of a barrier to dissociation for this state in the present work is consistent with the fact that the BiH molecule can be formed in this state by a recombination process, so this aspect of the calculations seems to be verified by the available experiment data. As with $X0^+$, it is found that the computed equilibrium bond length is too high, in this instance by 0.071 Å, a slightly greater error than for $X_1 0^+$ (Table III). The calculations correctly predict a slight decrease in this quantity upon the $B-X_1$ transition, and a similar result is also found in Ref. 12. The present computed ω_e value is too low by 23 cm⁻¹, in somewhat better agreement with experiment than is the case for $X_1 0^+$. The computed $B-X_1 T_e$ value is 22 496 cm⁻¹,

which is 1233 cm⁻¹ too high compared to the observed result.³²

There is also an important qualitative difference between the present potential curve (Fig. 2) for the third 0^+ and that reported by Balasubramanian.¹² We find a shallow minimum at $r=2.283$ Å (Table III) followed by a potential maximum near $r=2.65$ Å, whereas in the earlier theoretical treatment¹² a shoulder is present near $r=2.1$ Å, followed by a relatively steep drop until a very shallow minimum is formed for $r=2.6$ Å prior to approaching the $^2D_{5/2}$ dissociation limit. The next 0^+ state observed experimentally is $E^{5,6}$ and its molecular constants fit in well with those computed for $0^+(III)$ in the present CI study. However, in Ref. 12 the fourth computed root is identified with the E state. Our T_e value for $0^+(III)$ is only 424 cm⁻¹ above the observed value (Table III), whereas with the $0^+(IV)$ assignment of Ref. 12 an overestimation of 5840 cm⁻¹ must be assumed. The present r_e value of 2.283 Å is 0.106 Å larger than the corresponding measured value, but this error is only 0.04 Å larger than for the $X_1 0^+$ ground state and thus is reasonably consistent with other results of the present study. Again the $0^+(IV)$ assignment of Ref. 12 must allow for a much larger deviation from the observed value (0.33 Å).

The shallow minimum for the $0^+(III)$ potential curve (Fig. 2) is sufficient to hold two bound levels. Experimentally⁶ the $v'=2$ level for the $E0^+$ state is characterized by the disappearance of rotational levels, which result has been interpreted by Lindgren and Nilsson as a strong predissociation effect caused by the intersection of another (repulsive) curve. Inspection of Table II shows that $0^+(III)$ has the $\sigma\pi^3\Pi \lambda$ -s state as its major component at $r=3.0 a_0$ and then changes over to being primarily the

TABLE IV. Comparison of the present calculated $E0^+(v')-X_10^+(v'')$ vibrational transition energies ΔE (in cm^{-1}) with corresponding measured values of Lindgren and Nilsson (Ref. 6).

v'	v''	ΔE	
		Calculated	Observed
0	0	33 200	32 690
1	0	34 410	33 800
2	0	35 630	34 821
0	1	31 700	31 080
1	1	32 920	32 168

$\sigma^2\pi\sigma^* {}^3\Pi$ species at somewhat larger separations. The $b {}^1\Sigma^+$ also makes a large contribution at still greater r values, but at $r=5.25 a_0$ the main constituent is the repulsive $2 {}^3\Sigma^-$ state arising from the $\sigma\pi^2\sigma^*$ configuration. The latter's repulsive character fits in well with the interpretation in Ref. 6.

More quantitative evidence for the correctness of the present assignment for the $E0^+$ state as $0^+(\text{III})$ can be obtained by comparing the computed $E-X_1$ vibrational transition energies with those reported experimentally by Lindgren and Nilsson (Table IV). For this purpose the $E0^+$ adiabatic vibrational frequency given in Table III has been employed to obtain an estimate for the lowest unbound levels of this state. A complex coordinate treatment based on the corresponding diabatic potential curves which may be constructed from the adiabatic $0^+(\text{III})$ and $0^+(\text{IV})$ data could be used to obtain an estimate of the predissociation lifetime as well, similarly as has been done in a recent theoretical treatment³⁴ of metastable states of the O_2 molecule. There is a strikingly good correlation between these two sets of results, with the calculations uniformly overestimating the observed energy differences by roughly 600 cm^{-1} . The computed barrier to recombination of 1840 cm^{-1} (Fig. 2) also is consistent with the failure to observe emission from the $E0^+$ state despite extensive effort to do so in the experimental study.⁶ The lack of such a barrier in the $0^+(\text{IV})$ potential curve of Ref. 12 is not obviously consistent with the above experience. Lindgren and Nilsson⁶ have suggested that a weak predissociation by a state with $\Omega \neq 0$ might be responsible for this effect. Such a rotational predissociation process should be less significant for low J values, however, and there is no evidence for such an effect.

The present computed vibrational frequency for the $0^+(\text{III})$ state is too high by 109 cm^{-1} , but this result may be caused by the failure to take nonadiabatic effects into account in the computations. Because of the sharply avoided crossing with the $0^+(\text{IV})$ potential curve in the neighborhood of the barrier discussed first (Fig. 2), it can be expected that the adiabatic picture is not as suitable for obtaining quantitative results as for the B and X_1 states at lower energy. The ω_e value for $0^+(\text{IV})$ in Ref. 12 is 106 cm^{-1} smaller than the measured $E0^+$ result. Our conclusion remains that the $0^+(\text{III})$ state computed in the present work is a good match for the experimental $E0^+$

species, as is perhaps most easily seen when attention is directed to the results of Table IV.

The predissociation of the $E0^+ v'=2$ level allows one to compute the dissociation energy of the BiH system, but again the value obtained depends on a number of assumptions which need to be made. Lindgren and Nilsson⁶ arrived at a D_0 value of $23\,412 \text{ cm}^{-1}$ (2.90 eV) by subtracting the ${}^2D_{3/2}$ term value (relative to the ${}^4S_{3/2}$ ground state) of $11\,419 \text{ cm}^{-1}$ (Ref. 35) from the observed $2-0 E-X_1$ transition energy of $34\,831 \text{ cm}^{-1}$ (Table IV). This procedure has been criticized in earlier work,¹² primarily because the $E0^+$ state must dissociate to the ${}^2D_{5/2}$ state of the bismuth atom rather than ${}^2D_{3/2}$, a difference of 4019 cm^{-1} .³⁵ In addition it overlooks the possibility that a barrier to recombination exists, which in the present work has been computed to be 1840 cm^{-1} (Fig. 2). On this basis one arrives at a lower D_0 value of $17\,553 \text{ cm}^{-1}$ (2.18 eV). The corresponding D_e value is then obtained with the aid of the observed $X_10^+ \omega_e$ value (1699.5 cm^{-1}) as $18\,402 \text{ cm}^{-1}$ (2.28 eV). The present calculations yield a value of $16\,008 \pm 500 \text{ cm}^{-1}$ ($1.98 \pm 0.06 \text{ eV}$), where the error bars are based on distinctions in the energies of the five Ω states which correspond to the ${}^4S_{3/2}$ limit for quite large r values. Balasubramanian¹² has computed a D_e value of 2.17 eV and in later work, Dai and Balasubramanian¹⁹ have reported a somewhat lower value of 1.80 eV . Dolg et al.¹⁸ have also given several results (2.06 and 2.14 eV) for this quantity, based on a different RECP, which are quite consistent with the present calculations. An error of 0.1 – 0.2 eV , especially an underestimation, of such a D_e value is typical accuracy for CI calculations carried out at the present level, so this kind of agreement is quite supportive of the above interpretation of the experimental data.⁶

The fourth 0^+ root in the present calculations exhibits a shoulder and then a minimum at somewhat larger r values, and thus more closely resembles the $0^+(\text{III})$ state of Ref. 12. As mentioned above, the potential minimum in question arises because of a sharply avoided crossing and thus this state is likely to be of little consequence in spectroscopic investigations. The fifth 0^+ state in the present study looks very much like the fourth 0^+ species of Ref. 12, which has been assigned therein to the $E0^+$ system experimentally observed. In general, since both the present and former¹² theoretical study agree that there are five key λ - s states leading to $\Omega=0^+$ eigenstates, it seems clear that at least for a good range of r values a like number of final states should result after introduction of the spin-orbit interaction in the CI treatment, as has been found in our work. Table II shows that the $0^+(\text{IV})$ state starts out at small r values to consist primarily of the $\sigma^2\pi\sigma^* {}^3\Pi \lambda$ - s state. It goes over to primarily $\sigma\pi^3 {}^3\Pi$ at $r \approx 3.5 a_0$ (first avoided crossing) and then to the $\sigma\pi^2\sigma^* 2 {}^3\Sigma^-$ at $r \approx 4.5 a_0$ (second crossing).

The $0^+(\text{V})$ state begins as $2 {}^3\Sigma^-$ but for $r \approx 4.0 a_0$ it takes on a significant amount of both the ${}^3\Pi \lambda$ - s states' character plus a similarly large contribution from $b {}^1\Sigma^+$. The latter state might be involved in the ${}^1\Sigma_x^- \rightarrow {}^1\Sigma_y$ transition reported by Heimer and Hulten in their early work,¹ in which case one must assign the lower electronic state to

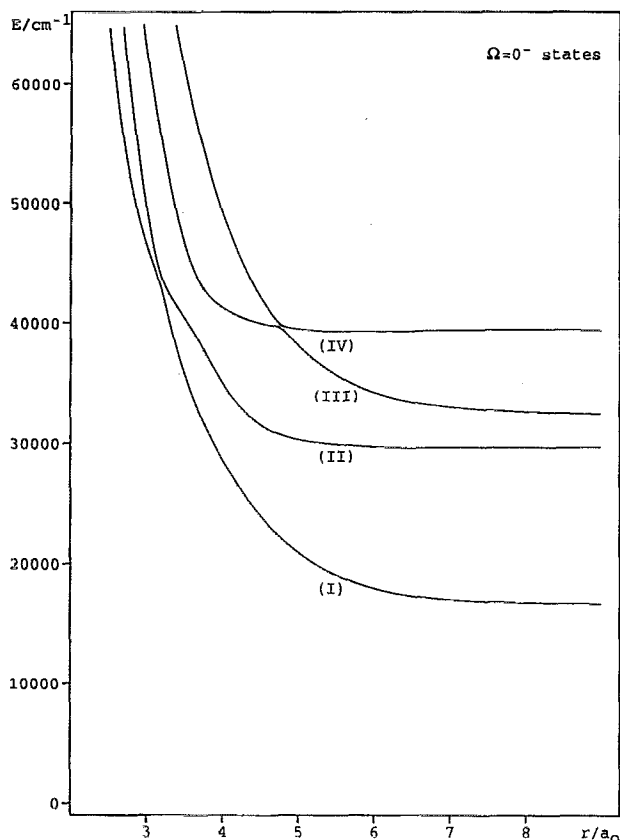


FIG. 3. Computed potential energy curves for the four lowest $\Omega=0^-$ states of the bismuth hydride molecule.

BO^+ . It will be shown below in Sec. IV that the radiative transition probability for this process is fairly high. Such an assignment is made plausible by comparing the present computed T_e value of the $0^+(V)-B$ transition ($20\,899\text{ cm}^{-1}$) with the observed¹ energy difference of $20\,647\text{ cm}^{-1}$ (Table III). On the other hand, the corresponding calculated bond lengths of the upper and lower states of 2.27 and 1.85 Å , respectively, do not match the corresponding measured value of 2.09 and 1.97 Å very well. In particular, the measured BO^+ r_e value of 1.7795 Å (Table III) is considerably smaller than that given for the lower state in the above transition. The fact that an avoided crossing is involved in the formation of this electronic state also suggests the possibility of significant predissociation of its low vibrational levels. Nonetheless the present work does indicate that the $0^+(V)$ state may have a stable potential minimum, which is consistent with the occurrence of transitions to the lower BO^+ state, and thus it would seem of interest to undertake a new search for the reported band system by means of more modern experimental techniques.

2. States with $\Omega=0^-$

The computed potential curves of the lowest four BiH states of 0^- symmetry are shown in Fig. 3. Unlike their 0^+ counterparts they possess no minima and appear to have very little influence on the appearance of the molecular

TABLE V. Composition of the lowest 0^- and 2 states of BiH (c^2 , %) at various bond distances r (in a_0). The leading configuration for each λ -s state is also shown.

State	r	$1^1\Delta$ $\sigma^2\pi^2$	$1^3\Pi$ $\sigma\pi^3$	$2^3\Pi$ $\sigma^2\pi\sigma^*$	$1^5\Sigma^-$ $\sigma\pi^2\sigma^*$	$1^3\Delta$ $\sigma\pi^2\sigma^*$
0^-	2.50	90.1	8.1
	3.50	91.1	4.3	2.5	0.3	...
	5.00	30.4	2.7	26.0	36.2	3.0
2 (II)	2.50	8.2	89.9	0.3
	3.50	5.9	77.6	2.8	10.4	1.6
	5.00	58.9	2.1	0.3	36.2	0.2
2 (III)	2.50	62.5	32.7	2.4
	3.50	0.8	...	43.5	40.2	1.1
	5.00	1.3	15.1	6.7
0^- (I)	2.50	...	98.7	...	0.1	...
	3.50	...	11.5	65.7	15.8	...
	5.00	...	8.6	8.4	70.7	...
	6.00	...	5.6	5.5	75.6	...

spectrum. The λ -s composition of the lowest 0^- state is described in Table V. At short r values it is primarily $\sigma\pi^3$ $^3\Pi$ but it eventually changes over successively to being predominantly $\sigma^2\pi\sigma^*$ $^3\Pi$ and then $\sigma\pi^2\sigma^*$ $^5\Sigma^-$. Thus two distinct crossings occur but they are so strongly avoided that almost no evidence of them can be seen from the shape of the potential curve itself. Each of the four 0^- states shown in Fig. 3 goes to a different bismuth atom dissociation limit. Only the lowest 0^- state has been treated in Ref. 12 and the appearance of this computed potential curve is very similar to that obtained in the present study.

3. States with $\Omega=1$

Potential curves calculated for the eight lowest $\Omega=1$ states of the BiH molecule are shown in Fig. 4, along with the corresponding curve for the lowest state of $\Omega=3$. For each of the lowest three bismuth atom asymptotes there are two convergent $\Omega=1$ states as expected for $\Omega=5/2$ and $3/2$ species in combination with the $^2S_{1/2}$ hydrogenic ground state. The $\Omega=3$ state also converges to the $^2D_{5/2}$ asymptote. The other two $\Omega=1$ curves correlate with $^2D_{1/2}$ and $^2P_{3/2}$ atomic states, respectively. A still higher lying $\Omega=1$ state which also converges to $^2D_{3/2}$ has been omitted from the present calculations.

The lowest eigenstate of this group is the X_21 component of the $^3\Sigma^-$ BiH ground state (often referred to as $A1$ elsewhere in the literature). Its λ -s composition is described in Table VI and is seen to be predominantly $X^3\Sigma^-$ until fairly large r values, for which the $\sigma^2\pi\sigma^*$ $^3\Pi$ states make significant contributions. A slight decrease in the equilibrium bond distance is observed (0.014 – 0.017 Å)^{8,32} relative to X_10^+ (Table III) and this result is mirrored in the present calculations, as well as in the earlier work of Ref. 12. The present computed zero-field X_2-X_1 splitting is 12% too low, whereas the analogous result is overestimated by 17% in Ref. 12. This splitting decreases to zero at large distances, since both states have a common dissociation limit. The most interest in X_21 experimentally centers around the fact that it is the final state in a number of

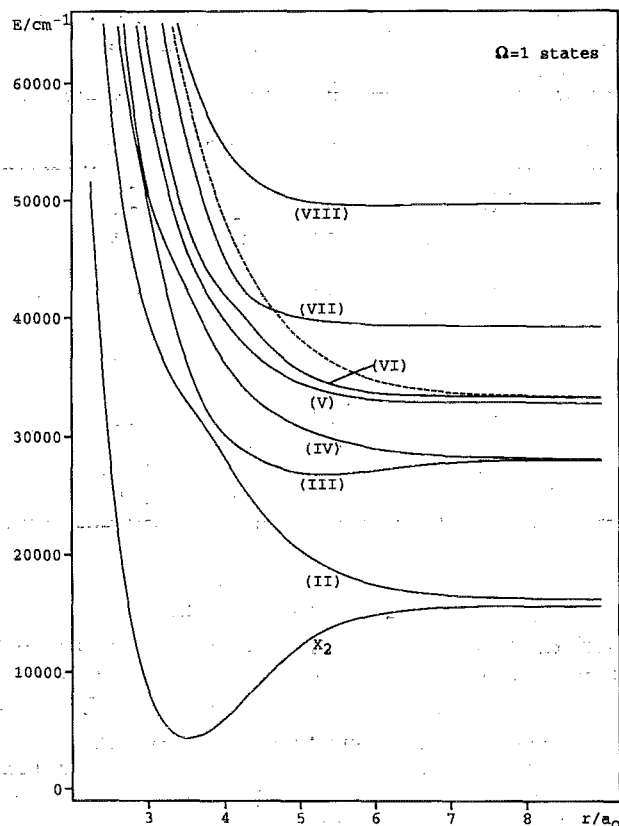


FIG. 4. Computed potential energy curves for the eight lowest $\Omega=1$ states of the bismuth hydride molecule. The dashed curve corresponds to the lowest $\Omega=3$ state of the system.

emission processes, as will be discussed in the following section, in which results for radiative transition probabilities are discussed.

The 1 (II) state has a repulsive potential curve (Fig. 4) and also dissociates to the $^4S_{3/2}$ asymptote. At short r values it is predominantly $\sigma\pi^3^3\Pi$ but it gradually takes on more $\sigma\pi^3^1\Pi$ character, before eventually changing to have its largest contribution from the $^5\Sigma^- \lambda-s$ state. The higher-lying $\Omega=1$ states are also repulsive, except for the 1 (III) species. It shows a minimum at $r=2.823 \text{ \AA}$ with a relatively small ω_e value of 559 cm^{-1} . The corresponding T_e value is computed to be 4239 cm^{-1} higher than for the

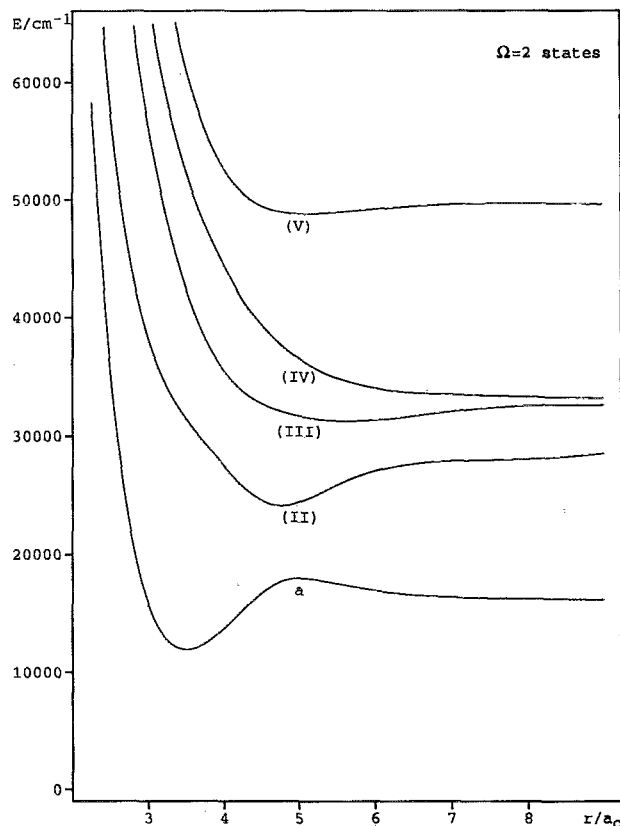


FIG. 5. Computed potential energy curves for the five lowest $\Omega=2$ states of the bismuth hydride molecule.

$B0^+$ state. The $\Omega=3$ state stems from the $\sigma\pi^2\sigma^*^3\Delta \lambda-s$ state and its potential curve is also repulsive.

4. States with $\Omega=2$

The final group of BiH states considered in the present study have $\Omega=2$ and their calculated potential curves are shown in Fig. 5. The lowest is $a2$ and it possesses a computed minimum at $r=1.855 \text{ \AA}$, very nearly the same as for the X_21 and $B0^+$ (Table III). Its $\lambda-s$ composition is also sketched in Table V, from which it is clear that at least one crossing occurs. It is strongly avoided and involves a transfer from $\sigma^2\pi^2$ character at short r values to predominantly $^5\Sigma^-$ near the dissociation limit. As a result there is a fairly

TABLE VI. Composition of the lowest 1 states of BiH (c^2 , %) at various bond distances r (in a_0). The leading configuration for each $\lambda-s$ state is also shown.

State	r	$1^3\Sigma^-$ $\sigma^2\pi^2$	$2^3\Sigma^-$ $\sigma\pi^2\sigma^*$	$1^3\Pi$ $\sigma\pi^3$	$2^3\Pi$ $\sigma^2\pi\sigma^*$	$1^1\Pi$ $\sigma\pi^3$	$2^1\Pi$ $\sigma^2\pi\sigma^*$	$1^5\Sigma^-$ $\sigma\pi^2\sigma^*$
X_21	2.5	95.1	...	2.0	...	1.5
	3.5	95.1	...	1.0	0.8	0.8	0.9	...
	5.0	85.3	...	0.2	4.3	0.3	0.6	0.5
1 (II)	2.5	3.2	...	82.5	...	12.5	...	0.1
	3.5	2.5	...	58.9	2.8	23.9	1.0	5.2
	5.0	1.1	3.5	1.6	10.7	4.9	0.7	64.1
	6.0	1.8	3.5	1.5	8.1	3.5	0.6	67.3

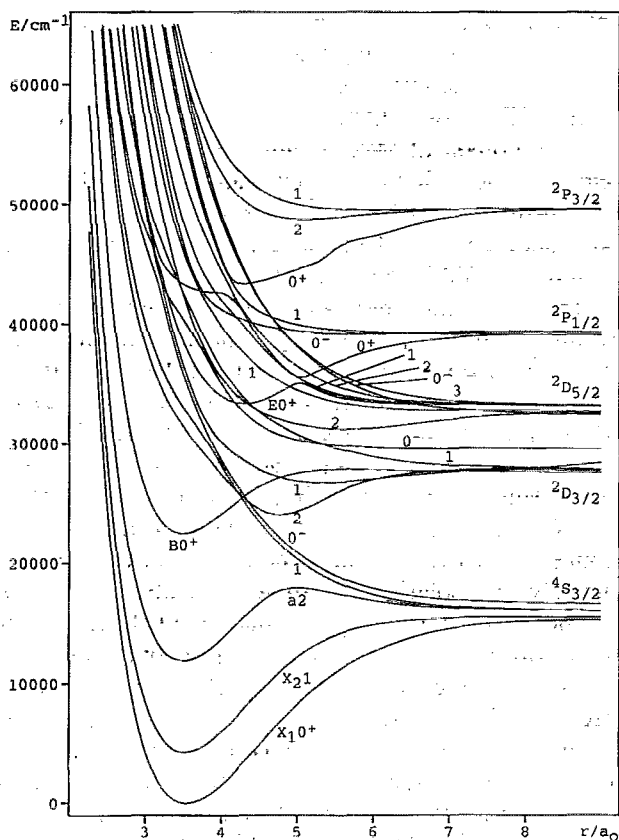


FIG. 6. Composite potential energy diagram for the 23 lowest-lying electronic states of the bismuth hydride molecule in the present theoretical treatment including spin-orbit coupling. The atomic dissociation limits correspond to $\text{H } ({}^2S_{1/2}) + \text{Bi}$ (as indicated).

large barrier to recombination in this state, similarly as has been found in earlier work.¹² The a_2 state has not been found experimentally as yet, as will be discussed in Sec. IV. The present calculated $a_2\text{-}X_1^0+$ T_e value of 11 906 cm^{-1} (Table III) may be compared with the corresponding result of 13 469 cm^{-1} computed in Ref. 12.

The $2(\text{II})$ state results from the same avoided crossing and is found to possess a fairly deep potential well (Fig. 5) with an r_e value of 2.521 Å and a fairly large ω_e value of 1013 cm^{-1} . The latter result is computed to be nearly 50% larger in Ref. 12, although the bond length is only 0.06 Å greater in that study. Its T_e value falls between that of $B0^+$ and $1(\text{III})$ according to the present calculations. From Table V it is seen that the $2(\text{II})$ state is predominantly $\sigma\pi^3 {}^3\Pi$ at short distances, changing to a mixture of $\sigma^2\pi^2 {}^1\Delta$ and ${}^5\Sigma^-$ to the right of the avoided crossing on the way to its dissociation limit (${}^2D_{3/2}$). It seems possible that transitions from this state from its potential minimum to lower levels of another electronic state might be observable, but it seems clear that only relatively high a_2 and X_2^1 vibrational levels can be reached with high intensity (Sec. IV). Finally each of the other three states in Fig. 5 is seen to be at most weakly bound, with the first two of these converging to the ${}^2D_{5/2}$ limit and the highest going to ${}^2P_{3/2}$.

TABLE VII. Comparison of calculated and measured term values T (in cm^{-1}) for the lowest states of the bismuth atom. The computed results stem from a spin-orbit CI treatment of the BiH molecule at $r=9.0 a_0$.

Atomic state	T	
	Calculated	Observed ^a
$4S_{3/2}$	0	0
${}^2D_{3/2}$	11 987	11 419
${}^2D_{5/2}$	16 866	15 437
${}^2P_{1/2}$	23 240	21 661
${}^2P_{3/2}$	33 568	33 164

^aReference 35.

5. Composite potential diagram

To put the results of the previous subsections in perspective, a composite diagram is given in Fig. 6 which contains all 23 Ω -state potential energy curves computed in the present study. The formation of the bismuth atom asymptotes is clearly seen from these results. All converging states for the $4S_{3/2}$, ${}^2D_{3/2}$, ${}^2D_{5/2}$, and ${}^2P_{1/2}$ atomic levels have been included in the present calculations, while only three of the five Ω components for the ${}^2P_{3/2}$ limit have been obtained (0^- and one 1 state are missing in this case). Based on the results computed for $r=9.0 a_0$, estimates for the atomic term values have been listed in Table VII for comparison with the corresponding measured values.³⁵ In each case there are from three to nine separate energies, whose values deviate by at most 500 cm^{-1} from the corresponding averaged value of a given atomic energy. The computed ${}^2D_{3/2}$ term value is overestimated by 568 cm^{-1} on this basis, while for ${}^2D_{5/2}$ the error is 1429 cm^{-1} . A somewhat larger discrepancy occurs for ${}^2P_{1/2}$ (1579 cm^{-1}), whereas the ${}^2P_{3/2}$ result is only in error by 404 cm^{-1} . These data indicate that the goal of size consistency is attained to a good level of accuracy in the present relativistic CI treatment. At the same time they give a clear indication of the reliability of the RECP employed in the present study.²²

Three of the $4S_{3/2}$ Ω states are seen to be bound, whereas for ${}^2D_{3/2}$ only the $B0^+$ and $1(\text{III})$ species have this characteristic. The $1(\text{II})$ state is in a position to cause rotational predissociation of the higher $B0^+$ levels. The barrier to recombination for the $E0^+$ state is seen to occur in a region where several potential curves of $\Omega \neq 0^+$ are crossing. The minimum in the $2(\text{III})$ potential curve occurs at only a slightly lower energy than for $E0^+$. The $v'=2$ level of $E0^+$ has been shown to be strongly predissociated⁶ and thus to provide a means of estimating the D_e value for the BiH ground state. A recombination barrier has been found in the present work, however, which should be taken into account in any such determination. Above the $E0^+$ state the most interesting feature seems to be the minimum in the $0^+(V)$ state. It should be subject to rotational predissociation by the $1(\text{VII})$ state according to the present calculations. In Sec. IV we will consider results for vibrational transition probabilities, especially those involving bound upper states.

TABLE VIII. Electric dipole moment values μ (in ea_0) of various states ($v=0$) of the BiH molecule computed in the present theoretical treatment. All values correspond to Bi^+H^- polarity.

State	μ
X_10^+	0.3760
X_21	0.2710
$a2$	0.2252
$B0^+$	0.1269
$2(\text{II})$	0.2551
$E0^+$	0.7924
$0^+(\text{IV})$	0.3653

IV. TRANSITION MOMENTS AND RADIATIVE LIFETIMES

A. Electric dipole moments

As discussed in Sec. II, electric dipole moment matrix elements have been computed for various combinations of Ω states and these data are averaged for different pairs of vibrational states. The corresponding electric dipole moments for the $v=0$ state in each case are collected in Table VIII for a number of key BiH electronic states. The X_10^+ ground state is computed to have a dipole moment of $0.376 ea_0$ ($2.541 \text{ D}/ea_0$), with a Bi^+H^- polarity. This result agrees quite well with a Dirac–Hartree–Fock value reported earlier²⁰ of $0.358 ea_0$. The corresponding X_21 value is $0.105 ea_0$ smaller in magnitude, so the effects of spin-orbit coupling are far from negligible. More generally it is seen that the values decrease with excitation energy for the first four electronic states, so that for $B0^+$ a value of only $0.127 ea_0$ is found (always with negative H atom polarity). This trend is strongly reversed for the $E0^+$ state, however, for which the largest dipole moment ($0.792 ea_0$) is obtained among all species treated. This result is a manifestation of the hydrogenic character of the σ^* MO, which is strongly occupied in this state near its equilibrium bond length (Table II). The dipole moments of two other $v=0$ levels have been computed [$0^+(\text{IV})$ and $2(\text{II})$] and these values are again rather similar to that obtained for the ground state. In summary, there is a strong tendency to favor Bi^+H^- polarity in all of the low-lying bismuth hydride states, but large dipole moments are most likely to occur only when the σ^* MO is strongly occupied.

B. Transition moments

Electric dipole transition moments for a series of low-energy processes are given as a function of internuclear distance in Table IX. The lower state is either X_10^+ or X_21 in each case. These results are also averaged for various combinations of vibrational functions and corresponding values for radiative transition probabilities and (partial) lifetimes of upper states (defined as sums over transition probabilities to all lower-lying vibrational states) are computed on this basis, as summarized in Table X. The X_21 state is computed to have a relatively long lifetime of 16.1 ms. Its transitions to X_10^+ become allowed after the inclusion of spin-orbit coupling but the relatively small energy separation keeps this process from occurring with high

probability [see Eq. (1)]. Fink *et al.*²⁷ have studied this transition but remark only that it is of weak intensity. The $a2$ state is next lowest in energy and it is computed to have a significantly shorter lifetime of 0.545 ms. Only transitions to X_21 are dipole-allowed in emission. On this basis there seems to be hope that the $a2$ state can be observed in future experiments, in which case the $0-0 a2-X_21$ transition is a good candidate for detection. According to Table III this transition should be found near 7600 cm^{-1} .

The $B0^+$ state undergoes relatively strong emission processes to both X_10^+ and X_21 . The present calculations indicate that the parallel transition ($\Delta\Omega=0$) is stronger than the perpendicular ($\Delta\Omega=1$). The corresponding partial lifetimes differ by a factor of 5 (Table X). The total lifetime of the $v=0$ level of the $B0^+$ state is computed to be $4.3 \mu\text{s}$, which is over 100 times shorter than for the $a2$ state, for example. The fact that the parallel transition is stronger in this case seems to be tied up directly with the relatively low polarity of bismuth hydride. Colin *et al.*³⁶ have noted that for Group V A diatomic halides there is a strong correlation between the mass ratio of the two atoms and their preference for either of these two transitions. Specifically for fluorides it is found that the perpendicular transition is the stronger of the two, i.e., in the case when the Group V A atom is heavier than the halogen. The opposite is invariably found to be true if the mass relationship is reversed. It has been argued elsewhere^{37,38} that this result can be at least partially understood on the basis of electronegativity arguments. When there is a large difference the dipole moments of the B and X states tend to be nearly equal and since the parallel transition moment is proportional to the difference of these quantities, there is a tendency for the perpendicular transition to dominate in this case. In the present example of bismuth hydride, we have already seen in Sec. IV A that although the electric dipole moments of this system are fairly small, there are still relatively large differences between different states, particularly between $B0^+$ ($0.127 ea_0$) and X_10^+ ($0.376 ea_0$), and this fact leads directly to the computation of a somewhat large transition probability between these two states. The BiH case thus falls into the same class as the Group V A halides in which the halogen atom is the heavier of the two constituents, and therefore fits in well with the empirical rules of Colin *et al.*³⁶

The state with the next highest T_e value (Fig. 6 and Table III) is $2(\text{II})$. The present calculations predict that although it has only a weak transition to the X_21 state (Table X), there is a relatively high probability for it to emit to $a2$ (partial lifetime of $12 \mu\text{s}$). Because of the large difference in equilibrium bond lengths of these two $\Omega=2$ states (Table III), however, it is likely that any intensity will be spread over a wide range of $a2$ vibrational quantum numbers. There is also a high probability that the molecule will dissociate in most cases, because downward vertical transitions from the $2(\text{II})$ potential minimum arrive at a point near the maximum in the $a2$ curve (Figs. 5 and 6). Apparently no $a2-2(\text{II})$ transitions have yet been observed experimentally, and it would appear the latter relationship is the main reason for this. Similar remarks hold for the

TABLE IX. Computed transition dipole moments μ (in ea_0) between X_10^+ , $B0^+$, $E0^+$, $0^+(IV)$, and X_21 states of the BiH molecule at various bond lengths r (in a_0).

r	μ				
	$B-X_1$	$E-X_1$	$0^+(IV)-X_1$	$B-X_2$	$E-X_2$
2.10	0.002 211	0.025 385	0.568 352	0.140 559	0.265 966
2.25	0.009 629	0.014 769	0.560 785	0.126 591	0.264 906
2.50	0.020 839	0.004 477	0.523 467	0.106 066	0.256 665
2.60	0.024 686	0.011 663	0.510 182	0.098 166	0.252 268
2.75	0.031 356	0.024 520	0.494 939	0.087 462	0.241 040
2.80	0.034 120	0.029 334	0.490 895	0.084 009	0.236 704
3.00	0.044 473	0.067 947	0.471 172	0.070 870	0.214 385
3.20	0.056 855	0.429 285	0.164 177	0.058 847	0.019 177
3.25	0.060 333	0.448 679	0.089 680	0.056 253	-0.019 504
3.40	0.072 195	0.447 743	0.034 552	0.048 373	-0.051 396
3.50	0.080 949	0.449 388	0.028 208	0.042 883	-0.060 307
3.60	0.090 804	0.444 523	0.027 996	0.037 283	-0.064 798
3.75	0.110 120	0.442 531	0.038 669	0.028 617	-0.070 733
3.90	0.134 080	0.437 353	0.055 958	0.019 074	-0.074 189
4.00	0.151 173	0.430 749	0.079 300	0.012 273	-0.075 510
4.10	0.173 723	0.427 678	...	0.004 423	-0.077 509
4.25	0.208 810	0.411 526	0.209 590	-0.006 564	-0.077 255
4.40	0.248 199	0.395 571	0.239 521	-0.018 533	-0.075 572
4.50	0.271 506	0.383 820	0.252 021	-0.025 385	-0.073 086
4.60	0.295 802	0.367 566	0.268 520	-0.032 217	-0.070 567
4.75	0.324 873	0.341 733	0.296 840	-0.040 047	-0.066 191
4.90	0.347 345	0.285 739	0.336 757	-0.044 854	-0.060 014
5.00	0.360 893	0.158 160	0.412 387	-0.046 879	-0.051 566
5.10	0.371 075	-0.105 764	0.428 020	-0.048 116	-0.025 570
5.25	0.379 667	-0.211 846	0.383 862	-0.048 311	-0.012 349
5.50	0.385 371	-0.223 271	0.355 266	-0.046 197	-0.010 042
6.00	0.346 954	-0.197 617	0.308 324	-0.036 977	-0.007 528
6.50	0.264 784	-0.153 847	0.213 900	-0.025 931	-0.003 475
7.00	...	-0.102 315	0.122 735
8.00	...	-0.029 338	0.028 318	...	-0.001 836
9.00	0.020 507	-0.007 505	0.006 482	-0.002 658	-0.000 916

1(III) state, which is calculated to possess a shallow potential minimum at $r=2.823$ Å (Table III and Fig. 6). In this case the strongest emission process is computed for the X_21 state, with a partial lifetime of $1.6 \mu s$ (Table X). Although there is apparently no recombination barrier for 1(III), there is still a low probability that such transitions will occur by virtue of the fact that the repulsive 1(II) state undergoes a sharply avoided crossing with 1(III) near its minimum, i.e., the latter state will be strongly predissociated as a result.

The $E0^+$ state is the next highest for which experimental data are clearly available in the BiH spectrum. As discussed in Sec. III B 1, there are at least two bound levels

for this state which have been reached in absorption studies^{5,6} involving the electronic ground state. The present calculations predict a partial lifetime for the parallel $E-X$ transition of only $0.12 \mu s$. The transitions to the X_21 and $B0^+$ states are also fairly strong. These results add further support to the $E0^+-X_10^+$ assignment of the vibrational transitions considered in Table IV. The fact that no comparable emission processes from the $E0^+$ state have been observed seems most easily explained in terms of the recombination barrier computed in the present study (Fig. 2), which prevents the molecule from being formed in this excited state under the experimental conditions employed.⁶

The $0^+(IV)$ state is also computed to have a relatively

TABLE X. Calculated radiative lifetimes (in μs) of excited states ($v'=0$) of BiH: Partial lifetimes τ_p for transitions to X_10^+ , X_21 , $B0^+$, and $a2$, respectively, and total lifetime τ .

State	$\tau_p(X_10^+)$	$\tau_p(X_21)$	$\tau_p(B0^+)$	$\tau_p(a2)$	τ
X_21	16 100	16 100
$a2$...	545	545
$B0^+$	5.2	24.3	4.3
$E0^+$	0.12	5.3	28.5	...	0.12
$0^+(IV)$	0.17	> 40	78	...	0.17
2(II)	...	660	...	12	12
1(III)	141	1.6	1.6

short radiative lifetime, primarily because of its transitions to X_10^+ . It seems unlikely that such an emission process can be observed, however, because of the sharply avoided crossing that $0^+(IV)$ undergoes with $E0^+$ near the location of its potential minimum. Finally the $0^+(V)$ state is computed to have a lifetime of $0.4 \mu s$ because of its high transition probability to the $B0^+$ state. It is also found to have strong transitions to X_21 , but weaker ones to X_10^+ . As discussed in Sec. III B 1, there is some reason for identifying the $0^+(V)-B0^+$ transition with a process observed by Heimer,² although this is far from certain based on examination of other characteristics such as the measured equilibrium bond distances of upper and lower states.

V. CONCLUSIONS

Relativistic CI calculations including the spin-orbit interaction have been carried out with the aid of an effective core potential for 23 states of the bismuth hydride molecule. Potential curves, vibrational wave functions, and transition probabilities have been computed and these results are found to give a consistent explanation for available spectroscopic data for this system. All Ω states which correlate with the 4S_u , 2D_u , and 2P_u dissociation limits have been studied except for two of the five states converging to $^2P_{3/2}$. The 0^+ states are the most interesting with reference to the experimental data and five such states have been calculated, consisting mainly of the $X^3\Sigma^-$, $b^1\Sigma^+$ λ -s states with a $\sigma^2\pi^2$ electronic configuration, two $^3\Pi$'s with $\sigma\pi^3$ and $\sigma^2\pi\sigma^*$ occupation, respectively, and the $2^3\Sigma^-$ species stemming from the $\sigma\pi^2\sigma^*$ configuration. The ground-state r_e value is overestimated by 0.06 \AA in the present theoretical treatment, and similar discrepancies are found for the various excited states for which experimental results have been reported. This level of accuracy is considerably better than observed for the BiF molecule²¹ employing a similar level of treatment, including the same RECP for the bismuth atom. There thus exists the possibility that the ionic bonding in the fluoride system is not as adequately described with this type of core potential²² as the more covalent type characterizing BiH.

The $B0^+$ excited state is found to dissociate without a barrier to the $^2D_{3/2}$ atomic state. A significant barrier was found in an earlier theoretical study,¹² but it is argued that the fact that the B state can be populated in recombination processes¹⁻³ speaks for the absence of such a potential maximum. Computation of transition moments for the $B0^+-X_10^+$ (parallel) and $B0^+-X_21$ (perpendicular) radiative processes indicates that the $\Delta\Omega=0$ band system is notably more intense. This result fits in well with empirical rules discovered by Colin *et al.*³⁶ for the relative strengths of Group V A halide transitions and indicates that the electronegativities of the two constituent atoms in each case play a key role in determining such relationships. Another bound excited state with nearly the same T_e value is the $2(II)$ species, but the calculations indicate that transitions from it to lower electronic states should be difficult to observe because of the bond length relationships between such pairs of states and also the likelihood of predissocia-

tion phenomena preventing such emission processes from occurring.

On the basis of the present calculations it is concluded that the experimental $E0^+$ state should be assigned to the $0^+(III)$ state. The present calculated spectroscopic constants are in good agreement with those found experimentally, e.g., and the computed magnitudes of the $E-X$ vibrational transition energies also fit in well with corresponding measured values (Table IV). This assessment differs from that reached in an earlier theoretical study,¹⁷ in which the fourth 0^+ eigenstate is identified with $E0^+$, but the agreement between calculation and experiment for that choice is considerably worse than found on the basis of the present interpretation. A barrier height in the order of 2000 cm^{-1} is computed for this potential curve, and this offers a simple explanation for the fact that no emission bands have thus far been observed from the $E0^+$ state. Since the experimental studies^{5,6} of this state involve recombination processes, it is argued that such a barrier would keep it from being formed so that such emission processes cannot occur.

The existence of a maximum in this potential curve also influences the calculation of the ground-state D_e value from available experimental data. Assuming that the $v'=2$ level of the $E0^+$ state has an energy near this maximum value, and also that the potential curve converges to the $^2D_{5/2}$ bismuth atom state, leads to a D_e value of 2.28 eV , which is 0.3 eV greater than the present computed CI result. In general, the CI energies of molecular states at larger r values which correspond to the same dissociation limit are found to agree to within $\pm 500 \text{ cm}^{-1}$ of their mean value, which is a clear indication of the degree to which the present theoretical treatment approaches the AO basis limit in each case. The corresponding computed atomic excitation energies overestimate the measured results by $500\text{--}1500 \text{ cm}^{-1}$. Finally, a number of other bound states are found in the present calculations and it is hoped that the information obtained for their potential curves and transition probabilities to other known states will aid in the further study of the BiH molecular spectrum.

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