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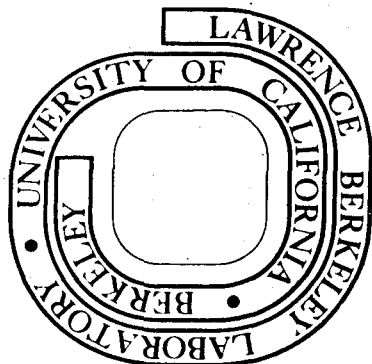
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PES OF ATOMIC AND MOLECULAR BISMUTH

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ABSTRACT

HeI photoelectron spectra of Bi and Bi_2 were recorded by study-
ing bismuth vapor at 750°C. The spectrum of Bi was found consistent
with a j-j coupling description of the ground state. However, relativ-
istic effects seemed to have little influence upon the relative photoion-
ization cross sections of the $^3P_{0,1,2}$ lines. Satellite peaks $^1D_2$ at
11.49 eV, and possibly also $^3D_{1,2}$ at 17.12 eV and $^3F_{2,3}$ at 17.47 eV
were observed. They were assigned to admixtures of the configurations
$[(6s_{1/2})^2 6p_{1/2}(6p_{3/2})^2]_{3/2}$ and $[6s^2 6p6d^2]_{3/2}$ into the main ground-state
configuration $[(6s_{1/2})^2(6p_{1/2})^2 6p_{3/2}]_{3/2}$. An autoionization process
at the energy of HeIγ radiation (23.74 eV) was suggested by the large
intensity of the HeIγ spectrum. The photoelectron spectrum of Bi_2
showed three distinguishable bands at 7.53 eV, 8.94 eV, and 9.30 eV
corresponding respectively to the ionic states $^2\Pi_{u,3/2}$, $^2\Pi_{u,1/2}$, and
$^2\Sigma_g^+$ due to ionization of a $(\pi_u 6p)$ or $(\sigma_g 6p)$ electron. A probable
fourth band was observed at 14.87 eV, and was tentatively assigned to
$^2\Sigma_u^+$ of Bi_2^+ formed from $(\sigma_u 6s)$ ionization. The spectrum of

Bi_2 was found similar to those of lighter Group VA diatomics. A relationship between the equilibrium internuclear distance and the difference between the binding energies of $(\sigma_g np)$ and $(\pi_u np)$ orbitals was established for the Group VA diatomics.

I.   INTRODUCTION

Recently photoelectron spectra of atomic vapors have been demonstrated[1-4] to be capable of providing unique information about electron correlation effects in the ground states of atoms. This is accomplished by observing directly in the spectra correlation satellite peaks due to configuration interaction in the initial state. The theory of correlation satellites has been extensively discussed,[5,6] and will not be reviewed here. In this paper, we present a photoelectron spectroscopic study of atomic bismuth, which also shows relativistic and correlation effects.

The photoelectron spectrum of Bi was obtained from bismuth vapor at $(750 \pm 20)°C$. In this temperature range the vapor consists of roughly equal amounts of Bi and Bi_2, with less than 1% of heavier species. Therefore, bismuth vapor also provides a chance to study Bi_2. As the heaviest stable diatomic molecule, Bi_2 provides an interesting case in which to study relativistic effects in molecular bonding. In the same context, it is interesting to compare the photoelectron spectrum of Bi_2 with those of other Group VA diatomic molecules.

II.   EXPERIMENTAL:

The experiments were carried out in a Perkin-Elmer PS-18 photoelectron spectrometer modified for high temperature work. The details of the modifications have been reported elsewhere.[2] The spectrum of bismuth was taken at $(750 \pm 20)°C$, as determined by an iron-constantan thermocouple. The sample was introduced in the form of small pieces of metal.

The composition of bismuth vapor has been well documented by

thermodynamic effusion methods, which indicate a Bi_2/Bi ratio of 1.5 at 800°C.[7-10] A recent ESCA study[11] of the $4f_{7/2}$ lines confirmed this ratio. From published thermodynamic data we estimated the dimer to monomer ratio under our experimental conditions as 1.7 ± 0.2. Our spectra were consistent with this value. No additional electron lines were detected which could be identified with any other species or known sample impurities. Energy calibration was done by introducing Ar and Xe together with the sample in a separate run. Peak areas were corrected for the change of the spectrometer transmission with electron kinetic energy using the approximate relation $\Delta E/E$ = constant. No other correction was made for inelastic scattering or charging effects.[12] Hence the area ratios reported here carry large experimental uncertainties. This is especially true for the molecular bands, which were broad and partially obscured by the atomic peaks.

III. RESULTS

The HeI photoelectron spectrum of Bi and Bi_2 is shown in Fig. 1. Assignments of atomic peaks were made by comparison of binding energies with optical data.[13] Some of the molecular lines of Bi_2 are easily distinguishable by their larger widths. This can be seen most clearly in Fig. 2, which depicts the portion of the spectrum between 6 and 11 eV binding energies. Additional identification was accomplished by noting the behavior of the line intensites with respect to the oven temperature. The intensities of the group of lines belonging to Bi_2 decreased with increasing temperature relative to that of atomic peaks, while the relative intensities within each group remained unchanged. In one experiment, the Bi vapor was superheated, and consequently only weak molecular lines were detected, thus confirming our identifications.

Table I summarizes the experimental results for both Bi and Bi_2.

The spectrum of atomic Bi ($6s^2 6p^3$: $^4S_{3/2}$) shows four main peaks at binding energies 7.29 eV, 8.94 eV, 9.40 eV, and 16.73 eV corresponding respectively to the ($6s^2 6p^2$: $^3P_0$), ($6s^2 6p^2$: $^2P_1$), ($6s^2 6p^2$: $^3P_2$) and ($6s6p^3$: $^5S_2$) states of Bi^+ and 3 additional weaker peaks at 11.49 eV, 17.12 eV and 17.47 eV corresponding to the ($6s^2 6p^2$: $^1D_2$), ($6s^2 6p6d$: $^3D_2$ or $^3D_1$) and ($6s^2 6p6d$: $^3F_2$ or $^3F_3$) states of Bi^+. The peaks designated by β or γ are from HeIβ (23.09 eV) and HeIγ (23.74 eV) radiation, and the peaks designated by HI and OI arise by photoionization to the $Bi^+(^3P_0)$ state by, respectively, the HI (10.199 eV) and OI (9.521) eV radiation that are present due to traces of H_2O.[14]

The spectrum of diatomic Bi_2 ($^1\Sigma_g^+$) shows three distinct bands at vertical binding energies 7.53 eV, 8.94 eV, and 9.30 eV corresponding respectively (see discussion) to the $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ states of Bi_2^+ resulting from ionization of the ($\pi_u 6p$) orbital and the $^2\Sigma_g^+$ state of Bi_2^+ from the ($\sigma_g 6p$) shell. A weaker line at 14.87 eV is also observed and tentatively attributed to Bi_2^+, since its intensity followed those of the other molecular lines. It is assigned to the $^2\Sigma_u^+$ state arising from ionization of the ($\sigma_u 6s$) orbital.

IV. DISCUSSION

A. Atomic Bismuth

In the photoelectron spectrum of Pb, Süzer et al.[2] reported satellite peaks due to admixtures of ($6s^2 6d^2$) and ($6s6p^2 6d$) configurations into the ($6s^2 6p^2$: $^3P_0$) ground state. Furthermore, it was confirmed that j-j coupling is appropriate for describing the ground state of Pb as a result of strong spin-orbit (s-o) interaction. Consequently,

the ground state is better approximated by $\Psi = a(6p_{1/2})^2_0 + b(6p_{3/2})^2_0$
with $a \gg b$, as predicted by relativistic calculations.[15] Being next
to Pb in the Periodic Table and thus having a slightly larger s-o
interaction, Bi $(6s^2 6p^3 : {}^4S_{3/2})$ is certainly expected to follow the
j-j coupling scheme closely. Therefore, the ground state of Bi can
be approximated as a simple CI expansion

$$\psi({}^4S_{3/2}) = a[(6s_{1/2})^2(6p_{1/2})^2(6p_{3/2})]_{3/2}$$

$$+ b[(6s_{1/2})^2(6p_{1/2})(6p_{3/2})^2_2]_{3/2} + c[(6s_{1/2})^2(6p_{3/2})^3]_{3/2}. \qquad (1)$$

The relative weights of a,b, and c depend on the magnitude of the s-o
coupling constant. Qualitatively, simply on energy grounds $(6p_{1/2}$ lies
lower than $6p_{3/2})$ and by analogy to Pb[2], one expects the coefficients
to fall in the order $a \gg b > c$. Furthermore, considering the near-
degeneracy of 6d and 6p shells, and again by analogy to Pb, one may
expect the ground state of Bi to have an admixture of configurations
arising from 6p → 6d excitations, e.g., $[6s^2 6p 6d^2]_{3/2}$.

Let us first concentrate on the main configuration in the ground
state, i.e. $[(6s_{1/2})^2(6p_{1/2})^2(6p_{3/2})]_{3/2}$. Removal of an electron from
the $6p_{3/2}$ shell gives one state ${}^3P_0$ (L-S designation) at 7.289 eV
and the removal of an electron from the $6p_{1/2}$ shell gives two states
${}^3P_1$, and ${}^3P_2$ (since the total J can couple to 1 or 2) at 8.942 eV and
9.401 eV, respectively. These three peaks are observed experimentally
in the ratio of approximately 1:3:5 (Table I), close to their statisti-
cal ratios. This is a bit surprising considering that now the $6p_{1/2}$
and $6p_{3/2}$ shells are rather different from each other because of large
s-o interaction [the calculated ⟨r⟩ values for $6p_{1/2}$ and $6p_{3/2}$ shells

are respectively 2.56 and 2.94 a.u from Ref. 15b]. This suggests that photoionization cross sections for these sub-shells are approximately the same, which agrees with the behavior of the 6p sub-shells of Pb[2], but contrasts with that of Hg 5d sub-shells[3,12] in which the observed ratio deviated from the statistical ratio. Perhaps angular distribution studies would clear up this point.

Removal of an electron from the 6s shell gives two states (again two possibilities for total J); only one of these ($^5S_2$) could be observed at 16.730 eV, the other ($^3S_1$) is expected to have a binding energy higher than 21.21 eV (see below). The intensity of the $^5S_2$ line is much lower than those of the 6p lines, again similar to the Pb case.

Turning to the secondary configurations in eq. 1, we note they can give rise to observable satellite peaks if their coefficients are large enough. Ionization of a $6p_{3/2}$ electron from $[(6s_{1/2})^2(6p_{1/2})(6p_{3/2})^2_2]_{3/2}$ gives the $^3P_1$ and $^3P_2$ state of Bi^+, but no new ionic states. However, the removal of the $6p_{1/2}$ electron gives the $[(6s_{1/2})^2(6p_{3/2})^2_2]_2$ state at 11.49 eV with the L-S designation of $^1D_2$, which can only arise in the spectrum through configuration interaction. The Bi^+ $6s^2 6p^2(^1S_0)$ state at 12.766 eV, which corresponds to $[(6s_{1/2})^2(6p_{3/2})^2_0]_0$ and would result from the removal of $6p_{3/2}$ electron from the last configuration in eq. 1, has not been observed. This confirms our expectation that the coefficient c is the smallest in eq. 1, because the configuration $[(6s_{1/2})^2(6p_{3/2})^3_{3/2}]_{3/2}$ involves two-electron excitation from the $6p_{1/2}$ sub-shell into the $6p_{3/2}$ sub-shell and is highly unfavorable on energy grounds. The corresponding configuration was not observed in the Pb spectra.[2]

A total of eight states are possible resulting from the ionization of a 6s electron from the secondary configurations in eq.(1). Only three of these states have been tabulated by Moore;[13] they are $^3D_1$, $^3D_2$, and $^3D_3$ with binding energies at 18.998, 19.058, and 19.198 eV respectively. We have carried out an intermediate coupling calculation for the $6s6p^3$ configuration, using the tabulated $F^2(6p,6p)$ and $G^1(6s,6p)$ integrals from Hartree-Fock calculations[15a] and the experimental s-o coupling constant of Bi 6p.[18] The binding energies of the remaining states, including $^3S_1$, were all estimated to be greater than 21 eV. Fig. 1 shows some indication for the presence of several additional peaks in the 19 - 20 eV region. However, due to poor transmission of the analyzer for the low energy electrons, unambiguous identification of these peaks is difficult, thus precluding any positive assignments of the $^3D_{1,2,3}$ lines.

At least two more lines are observed at 17.12 eV and 17.47 eV, corresponding respectively to $^3D_{1,2}$ and $^3F_{2,3}$ states of the $6s^26p6d$ configuration of Bi^+. They can originate from the $6s^26p6d^2$ configuration in Bi. This configuration is favorable because the 6d shell is near-degenerate with the 6p shell. Again similar configurations were found to mix with the main configuration, and to give satellite lines, in the Pb spectra.[2] In addition, there are six other states of the $6s^26p6d$ configuration of Bi^+ reported [13] at binding energy between 19.5 and 20.7 eV. These states may also contribute to the unidentified structure betwen 19 - 20 eV.

There are several anomalies in the intensities of the ^3P lines of Bi^+ ionized by HeIγ radiation, as shown in Fig. 1. In Table II we have listed the relative intensities of these lines excited by the different HeI resonance lines. It is known[14] that in a cold cathode discharge lamp such as that used in the Perkin-Elmer spectrometer, the HeIβ line normally amounts to ∿5% and the HeIγ line≲1% of the dominant HeIα radiation. Our own experience with this lamp confirms this. Therefore, the observed $^3P_{0,1,2}$ line intensities (Table II) produced by HeIγ radiation are unexpectedly large. They cannot reasonably be attributed to fluctuations of the lamp output, as they lie far outside any fluctuations in our experience. The observation was reproduced in three independent runs. By contrast, the molecular lines of Bi_2^+ produced by HeIγ radiation are hardly detectable (Fig. 1) as expected. The possibility of impurities was carefully checked and ruled out by using NeI radiation, where no corresponding lines were observed. The first anomaly is thus an enchanced overall intensity in the HeIγ spectrum. Secondly, the ratio of $^3P_0 : {}^3P_1 : {}^3P_2$ in the HeIγ spectrum is 1 : 1.1 : 1.2, substantially different from the statistical ratio 1 : 3 : 5, which seems to be followed by the HeIα

spectrum quite closely. The cause of the sudden rise of the ^3P line intensities at HeIγ radiation (23.74 eV) and their unexpected intensity ratio cannot be determined at the present. We note, however, this is the type of behavior expected if a resonant state of Bi resulting from $5d \rightarrow np$ or $n'f$ excitation is reached by HeIγ radiation, and if this state subsequently autoionizes to give the ^3P lines. Further study with a monochromatic light sources is needed to clarify this point.

The intensities in the HeIβ spectrum (Table II) appear to reflect the expected HeIβ radiation intensity. The observed ratio $^3P_0/^3P_1$, 1.5 seems to deviate appreciably from 1/3; however, the large experimental uncertainty precludes any definite conclusion.

B. Molecular Bismuth

From an analogy with N_2, P_2, etc., the ground-state valence electronic configuration of Bi_2 may be written as

$$(\sigma_g 6s)^2 (\sigma_u 6s)^2 (\sigma_g 6p)^2 (\pi_u 6p)^4 : {}^1\Sigma_g^+ ,$$

where $(n\ell)$ denotes the dominant components of each molecular orbital. Considering the large internuclear distance $(2.85Å)^{16}$ and the small vibrational frequency $(172.71 cm^{-1})^{17}$ of Bi_2, one expects the bonding between the two bismuth atoms to be weak, and the core electrons to contribute little to the bonding. Thus the valence photoelectron spectrum of Bi_2 would divide into two groups of bands; the first group arising from 6p MO's would be found close to the atomic ^3P lines and the second from 6s MO's close to $(6s)^{-1}$ lines. The removal of a $(\pi_u 6p)$ electron would give the s-o partners $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ in the first group, with $^2\Pi_{u,3/2}$ lower in energy. The separation between the $^2\Pi$ states would be close to the 6p atomic s-o coupling constant,

i.e. 1.25 eV,[18] as was found to be the case in diatomic halogens[19,20] and in diatomic chalcogens.[21-23] By analogy with N_2^+,[24] PN^+,[25] and P_2^+.[26] The $(\pi_u 6p)$ orbital would be comparatively bonding and thus the $^2\Pi$ bands of Bi_2^+ would be relatively broad due to vibrational structure whereas the other valence MO's would be comparatively nonbonding and give relatively sharp lines. With these considerations, it is rather a straightforward matter to assign the molecular spectrum of Bi_2. Thus, we assign the first two bands (at 7.53 and 8.94 eV respectively) separated by 1.4 eV and each with a width of $\sim$0.27 eV to the two $^2\Pi$ partners. The sharp line at 9.30 eV is assigned to the $(\sigma_g 6p)^{-1}$ state and the weak line at 14.87 eV to the $(\sigma_u 6s)^{-1}$ state. As pointed out in Section III, the identification of the latter state is only tentative. We note the $^2\Sigma_u^+$ state at 14.87 eV falls in the expected energy region, as the binding energy of the atomic 6s shell is about 16.8 eV and the binding energy of $(\sigma_u 6s)$ is expected to be lower than this value because of its slightly antibonding nature. The $(\sigma_g 6s)^{-1}$ state is however not definitely observed, presumably due to its small cross section (cf. the weak intensity of $^2\Sigma_u^+$), and/or its binding energy being higher than 21.21 eV.

In view of the large s-o interaction in bismuth, it is interesting to compare the spectrum of Bi_2^+ with those of the iso-valent molecules N_2^+,[24] PN^+,[25] and P_2^+.[26] For this purpose, we have collected the relevant data in Table III. We note the general appearance of the corresponding bands in every spectrum is strikingly similar in that only the $^2\Pi_{3/2,1/2}$ bands show appreciable width due to vibrational structure while the rest are relatively sharp peaks. This indicates that only the $(\pi_u np)$

molecular orbital is bonding while the other orbitals are relatively

nonbonding. While the general resemblance of the spectra is usually

expected from chemical similarity, the gradual crossover in energy

between the ionic states $^2\Sigma_g^+$ and $^2\Pi_u$ from N_2^+, PN^+, P_2^+, to Bi_2^+ (Table III)

requires comment.

The photoionization of N_2 to N_2^+, in which $^2\Sigma_g^+$ comes lower than the

$^2\Pi_u$ state, is the classical example of the breakdown of molecular orbital

ordering by Koopmans' theorem,[27] since Hartree-Fock MO calculations of

N_2 [28] invariably predict $(\pi_u 2p)$ as the highest occupied MO. Various

elaborate theoretical attempts[29] have been made to elucidate the cause

of the discrepancy, while Price[30] has given a simple physical explana-

tion. Price pointed out that the internuclear distance in N_2 is so

short as a result of its 'triple' bond that the two nuclei have been

pulled through some of the $(\sigma_g 2p)^2$ cloud and this orbital therefore

supplies no bonding energy at this separation. Consequently, for N_2

it takes less energy to remove a $(\sigma_g 2p)$ than a $(\pi_u 2p)$ electron. However,

going down the Periodic Table, the atomic valence orbitals become

larger, increasing the internuclear separation; therefore, the $(\sigma_g np)$

MO will be expected to become increasingly more stable with respect

to $(\pi_u np)$. The latter will eventually become the highest occupied MO

and the $^2\Pi$ state the ground ionic state, as observed (Table III). In

Fig. 3, the difference between the vertical binding energies of the

$(\sigma_g np)$ and $(\pi_u np)$ MO's (the mean of the $^2\Pi$ energies is taken for the

$(\pi_u np)$ orbital of Bi_2^+) is plotted against the internuclear distances

of the diatomics. An approximate linear relation is obtained.

From Fig. 3, it is seen that the crossover occurs at r_e ~1.9 Å. Therefore, for AsN with r_e = 1.618 Å,[31] the $^2\Sigma_g^+$ would be the ground ionic state whereas for As_2^+ and Sb_2, with r_e expected to be larger than that of P_2, the reverse would be true.

In spite of the large error in estimating the intensities of molecular lines, the reported $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio of ~1.5 is significantly different from 1, the expected statistical ratio. This value contrasts sharply with the value of 10 for the intensity ratio $X^2\Pi_{g,1/2}/X^2\Pi_{g,3/2}$ in Te_2, which Berkowitz[22,23] attributed to the photoeletron leaving predominantly in an np_σ channel. Recently, we[32] have advocated an alternative explanation based upon unequal population of the $\pi_{g,1/2}$ and $\pi_{g,3/2}$ MO's. In other words, the ground state of the π^2 configuration is better described as $\Psi = a(\pi_{g,1/2})^2 + b(\pi_{g,3/2})^2$ with $a^2 > b^2$, as a result of large s-o coupling. In our picture, the ratio of the $^2\Pi$ partners should be 1 as long as the molecule has a closed-shell configuration, whereas there is no a priori reason why the ratio for Bi_2 should be so much different from Te_2 according to Berkowitz's interpretation. On the other hand, the slight deviation of the ratio from 1 in Bi_2 may arise from a difference in the wavefunctions of the $\pi_{u,1/2}$ and $\pi_{u,3/2}$ MO's due to relativistic effects; a similar effect has been observed in Hg.[12] Finally, we note the intensity of the $^2\Sigma_g^+$ line relative to the $^2\Pi$ appears to be proportional to their statistical weights, while the extremely weak intensity of the $(\sigma_u 6s)^{-1}$ state is consistent with the intensity of the atomic $(6s)^{-1}$ peak.

V. CONCLUSIONS

The principal conclusions of this work can be stated as follows:

1. The HeI photoelectron spectrum of Bi was satisfactorily inter-pretated by describing the ground state of Bi in the j-j coupling scheme.

2. Within experimental accuracy, relativistic effects did not seem to have caused sufficient difference in the initial state wave function to affect the statistical intensity ratio, i.e., 1 : 3 : 5 of the $^3P_{0,1,2}$ lines.

3. The configuration-interaction satellite peaks $^1D_2$ at 11.49 eV and possibly $^3D_{2,1}$ at 17.12 and $^3F_{2,3}$ at 17.47 eV were observed.

4. An autoionization process occuring at the energy of HeIγ radia-tion (23.74 eV) was suggested by the spectra.

5. Despite the large s-o coupling, the photoelectron spectrum of Bi_2 followed the general trend of those of other lighter Group VA diatomics.

6. The difference in the binding energies of the $(\sigma_g np)$ and $(\pi_u np)$ MO's was found to vary linearly with the internuclear distances.

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Table I. Observed States of Bi^+ and Bi_2^+.

Ion	Final State		Apparent Relative Intensity[a]	Experimental FWHM[a] (eV)	Vertical Binding Energy[a] (eV)	Apparent Adiabatic Binding Energy(eV) [b]	Energy from Other Data (eV)
	$6s^26p^2$	$^3P_0$	100	0.075	7.29(3)		7.289[c]
		$^3P_1$	320(50)	0.08	8.94(3)		8.942
		$^3P_2$	510(40)	0.08	9.40(3)		9.401
	$6s^26p^2$	$^1D_2$	16(3)	0.07	11.49(3)		11.495
Bi^+	$6s6p^3$	$^5S_2$	26(5)	0.07	16.73(3)		16.730
	$6s^26p_{1/2}6d_{3/2}$	$^3D_2$		0.08	17.12(4)		17.090
		$^3D_1$	54(10)	—	—		17.274
	$6s^26p_{1/2}6d_{5/2}$	$^3F_2$		0.07	17.47(4)		17.457
		$^3F_3$		—	—		17.483

(Continued)

Table I. Observed States of Bi^+ and Bi_2^+. (Continued)

Bi_2^+	$(\sigma_u 6s)^2(\sigma_g 6p)^2(\pi_u 6p)^3$	$^2\Pi_{u,3/2}$	220(20)	0.27	7.53(3)	7.35(5)	7.1(3)[d]
		$^2\Pi_{u,1/2}$	340(50)	0.26	8.94(5)	8.65(5)	8.9
	$(\sigma_u 6s)^2(\sigma_g 6p)(\pi_u 6p)^4$	$^2\Sigma_g^+$	240(30)	0.09	9.30(3)	9.30(3)	——
	$(\sigma_u 6s)(\sigma_g 6p)^2(\pi_u 6p)^4$	$^2\Sigma_u^+$	4(2)	0.07	14.87(3)	14.87(3)	——

a) This work, with areas corrected for $\Delta E/E$ = Constant, with intensities given relative to $^3P_0$, taken as 100. Xe and Ar were used for calibration. Experimental errors are given parenthetically.

b) No correction for thermal population of vibrational levels in the ground state have been employed.

c) Optical data from Ref. 13.

d) Electron impact data from Ref. 9.

Table II. Relative Intensities ^{a} of $^3P_0$, $^3P_1$, and $^3P_2$ with Different HeI Lines.

Ion State	HeIα (21.22 eV)		HeIβ (23.09 eV)	HeIγ ^{c} (23.74 eV)	
$^3P_0$	100		3.0 (.5)	6.7 (1)	[1.0]
$^3P_1$	320	(50)	∿2 (1)	7.3 (1)	[1.1 (.1)]
$^3P_2$	510	(40)	b —	7.9 (1)	[1.2 (.1)]

$a)$ Areas corrected for $\Delta E/E$ = constant and normalized to $^3P_0$ (HeIα).

$b)$ This peak is overlapped by the $^2\Pi_{u,3/2}$ line of Bi_2^+; thus no estimate is possible.

$c)$ Values in square brackets are normalized to $^3P_0$.

Table III. Electronic Structure Data on the Diatomics of Group VA Elements.

Molecule	States	Vertical Binding Energy from PES (eV)	ω_e (cm^{-1})	Internuclear distance, r_e (Å)	Remarks
N_2 a	$^1\Sigma_g^+$	——	2359.61	1.094	——
N_2^+ b	$^2\Sigma_g^+(\sigma_g)^{-1}$	15.60	2340		Sharp, very little change in ω_e (Non-Bonding)
	$^2\Pi_u(\pi_u)^{-1}$	16.98	1810		Shows vibrational structure, large decrease in ω_e. (Bonding)
PN a	$^1\Sigma_{(g)}^+$	——	1337.24	1.491	——
PN$^+$ c	$^2\Sigma_{(g)}^+(\sigma_{(g)})^{-1}$	11.85	1200		Sharp (Non-Bonding)
	$^2\Pi_{(u)}(\pi_{(u)})^{-1}$	12.52	1050		Shows vibrational structure (Bonding)

(Continued)

Table III. Electronic Structure Data on the Diatomics of Group VA Elements. (Continued)

P_2	a	$^1\Sigma_g^+$	—	780.43	1.894	—
P_2^+	d	$^2\Pi_u(\pi_u)^{-1}$	10.65			Shows a vibrational structure, large decrease in ω_e (Bonding)
		$^2\Sigma_g^+(\sigma_g)^{-1}$	10.84			Sharp (Non-Bonding)
Bi_2		$^1\Sigma_g^+$	—	172.71 [g]	2.85 [h]	—
Bi_2^+	e	$^2\Pi_u(\pi_u)^{-1}$	$\begin{cases} 7.53 \ [\delta] \\ 8.94 \end{cases}$			Shows unresolved vibrational structure (Bonding)
		$^2\Sigma_g^+(\sigma_g)^{-1}$	9.30			Sharp (Non-Bonding)

a) Ref. 33   e) This work

b) Ref. 24   δ) Spin-orbit partners

c) Ref. 25   g) Ref. 17

d) Ref. 26   h) Ref. 16

FIGURE CAPTIONS

Fig. 1   The HeI photoelectron spectrum of atomic and diatomic bismuth.

Fig. 2   The expanded portion of Fig. 1 from 6 to 11 eV, showing the molecular lines of Bi_2.

Fig. 3   The plot of internuclear distances (r_e) vs the differences in the binding energies ($\Delta E_{B.E.}$) of the two lowest occupied MO's, $\sigma_g(p)$ and $\pi_u(p)$.
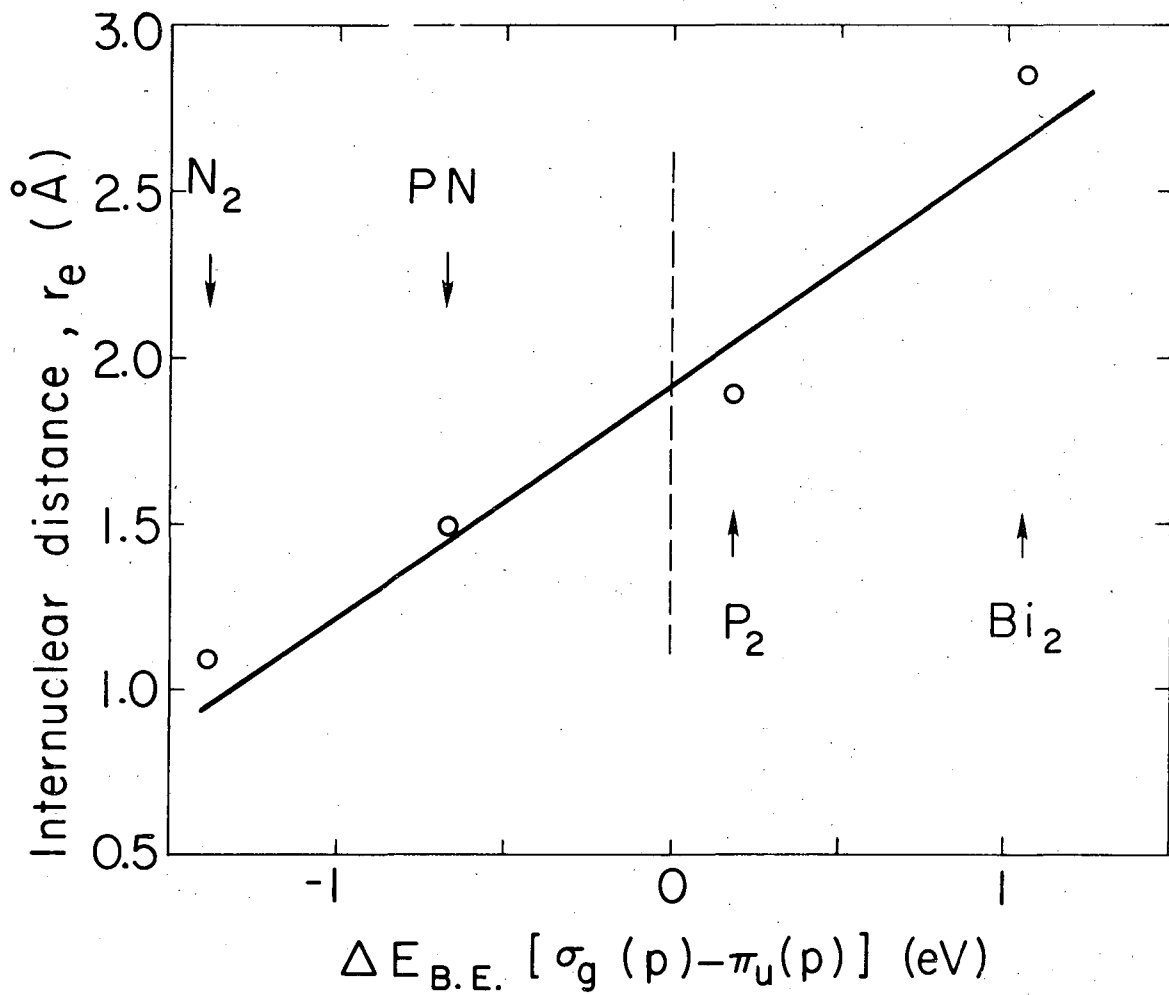
Fig. 1

XBL 762-2301

Fig. 2

XBL 761-2031

Fig. 3

XBL 762-2302

0 0 0 0 4 5 0 0 3 3 7 4