I. INTRODUCTION

We have recently reported on the vacuum ultraviolet photoionization spectra of As₂ and As₄. In that paper, we demonstrated the presence of two regions in the spectrum of As₂ where autoionization was prominent—two series converging to the A₂Σ⁺ state of As₂⁺, and a window resonance series converging to the B₂Σ⁺ state of As₂⁺. Both of these regions were shown to be analogous to corresponding series in the photoabsorption and photoionization of P₂. The window resonance series in As₂, attributed to excitation of electrons from the 4sₗ orbital, has been correlated with a window resonance series originating from the 4s orbital in atomic As. In fact, similar window resonance features have been observed stemming from excitation of the inner valence ns orbitals in each of the atoms of columns V–VIII and rows 2–4 of the periodic chart. Analysis of the series in As₂ enabled us to improve upon the photoelectron spectroscopic determination of the corresponding ionization potentials, and to deduce quantum defects for these series.¹

In the present paper, we present the photoionization mass spectra (PIMS) of the heavier pnictogen dimers Sb₂ and Bi₂. Elsewhere, we report on the trimers and tetramers of these elements, and on atomic bismuth.²

The He I photoelectron spectra (PES) of Sb₂ and Bi₂ were obtained recently at relatively high resolution by Wang et al.³ References to earlier, lower resolution PES studies are contained in that paper. The PIMS of Bi₂ in the threshold region has been reported by Saito et al.⁴ but as we shall see, the weak signal and low resolution in that work preclude the determination of an accurate adiabatic ionization potential or the elucidation of autoionization structure. To our knowledge, no prior PIMS studies of Sb₂ have been performed.

II. EXPERIMENTAL ARRANGEMENT

The photoionization apparatus utilized in these experiments was a reincarnation of an older apparatus. The essential components are a 1 m, normal incidence vacuum ultraviolet monochromator (McPherson), and a magnetic mass spectrometer. The sample is loaded into a Mo oven, and radiatively heated by a tungsten filament. The temperature of the oven is monitored by a Pt–Pt, 10% Rh thermocouple. The oven assembly is contained within an envelope formed by cooling shields, which allows the passage of the crude molecular beam effusing from the oven. The molecular beam is crossed by a selected bandwidth of the photon beam within an "open" ionization chamber situated above the shielded oven, and the resulting photoions are ejected by a repeller field. The molecular, photon, and ion beams are mutually orthogonal in space. The photoion beam is accelerated, focused by an electrostatic quadrupole lens, and mass analyzed. A particle multiplier pulse counts the ion signal, while a Ni photocathode monitors the light intensity. The analog photoelectric current is converted to voltage, and then to pulses by a voltage to frequency converter, and digitally counted. The wavelength response of the Ni photocathode had previously been calibrated. The wavelength resolution was adjusted for specific experiments between 0.83 and 2.5 Å FWHM. The saturated vapor above heated bismuth contains roughly comparable partial pressures of Bi and Bi₂, with Bi₁ and Bi₄ about two orders of magnitude less abundant. Hence, Bi₂ could be directly studied from such a source. However, antimony volatilizes almost entirely as tetramer. A satisfactory source of Sb₂ was obtained by vaporizing a mixture of InSb+In at a temperature of ~1000 K.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Sb₂

An overview of the spectrum between ~900 and 1500 Å appears in Fig. 1. The spectrum was also examined to a shorter wavelength, and it continues to decline to ~650 Å. In some runs, apparent window resonances were observed at ~890 and ~830 Å, but they were not reproducible, and hence are not shown. Near the threshold region (Fig. 1), autoionizing peaks are present. At 2.5 Å resolution, they appear to form a strong and a weak series, similar to that observed in As₂. However, at a resolution of 0.8 Å (see Fig. 2) a fine structure appears in the weak series, and perhaps also in the strong series.

The valence electronic configuration of Sb₂ is

\[ (σ₅S₂)²(σ₅5S₂)²(σ₅5P₂)²(π₅5P)⁴, \ X'1Σ⁺. \]
The He I photoelectron spectrum displays two broad peaks, followed by a sharp peak. The two broad peaks, with vertical ionization potentials (IPs) given as (8.7) and (9.1) eV, are assigned as 2P, 3/2 and 2P, 1/2, respectively, and correspond to the spin-orbit pairs formed upon removal of a π, 5p electron. The sharp peak, at 9.275 (5) eV, is assigned to 'X8+, formed upon removal of an electron from the π, 5p orbital. No vibrational fine structure was observed at this peak, but the resolution (stated to be 15 meV) may have been insufficient to resolve vibrational splittings, estimated to be about 25 meV.

The autoionizing peaks appearing in Figs. 1 and 2 can readily be assigned to two series converging on the 2Σ: limit, analogous to the pattern observed in P2 and As2. The electric dipole selection rules for the transition

\[ \text{Sb}_2(X '2:) + \text{hv} \rightarrow \text{Sb}^+( '2: , '11,) + \text{Sb}_2(2Σ, g) + e \]

require that the outgoing electron be odd (p, f, etc). If \( \text{Sb}^+_2 \) is described by a 2Σ, g core, then the Rydberg electron must also be odd. For \( \lambda_0 \), Carroll and Mitchell7 has assigned the "strong" series as \( p\sigma \), and the "weak" one as \( p\pi \), and we had retained this assignment. The fine structure appearing in Fig. 2 could conceivably be vibrational substructure in the Rydberg states, although other possibilities (\( J\) Rydbergs, spin–orbit splitting of \( np \) Rydbergs) exist. For the purpose of analysis by the Rydberg formula, we concentrate primarily on the strong series, which is easier to follow to higher \( n^* \) states, and also tends to be sharper.

In Table I, we list the wavelengths of the peaks in this series, and also the effective quantum numbers \( n^* \) for some alternative choices of series limits. Also shown in Table I are the leading (lowest energy) peaks in each weak series member, and the corresponding values of \( n^* \).

Wang et al.5 obtain 9.275 ± 0.005 eV for the IP to 2Σ, g, while Dyke et al.8 give 9.26 ± 0.01 eV. The \( n^* \) values shown in Table I clearly show a decline in the mantissa (a marked increase in the quantum defect \( \delta = n - n^* \)) when 9.275 eV is chosen as a limit. This is still true, although less so, with a 9.26 eV limit. If we neglect the last observable series member at 1359.5 Å, which is very sensitive to a slight change in \( \lambda \), then the most constant quantum defect, by least squares analysis, occurs for a series limit of 9.247 eV, with an estimated uncertainty of 0.003 eV. With this choice, the average quantum defect \( \delta = 3.672 ± 0.028 \). For the weak series, the quantum defect is 3.313 ± 0.028. Theodosiou, et al.9 have calculated atomic quantum defects for atoms in the Hartree–Slater approximation up to \( Z=50 \). A brief extrapolation to Sb (\( Z=51 \)) would appear to yield \( \delta_p \approx 3.35 \). Comparison with experiment10 suggests that the values of Theodosiou et al. may be slightly too low. Hence, our \( \delta_p \) and \( \delta_p \) appear to straddle the atomic \( \delta_p \), although in this case \( \delta_p \) seems to be closer to \( \delta_p \).

Donovan and Strachan11 have reported the observation of absorption bands in the vacuum ultraviolet attributed to \( \text{Sb}_2 \). By assuming quantum defects, they have deduced an IP(\( \text{Sb}_2 \)) ≈ 9.3 eV, which they believed to be the first ionization potential, corresponding to \( (p\pi)^{-1} \). It is very close.
to our deduced higher ionization potential, \((\rho_\sigma g)^{-1}\). Hence, one might expect to see some relation between the absorption spectra observed by Donovan and Strachan and the autoionizing members converging to \((\rho_\sigma g)^{-1}\) reported here. One region (\(\sim 1425\) Å) is common to both studies. Donovan and Strachan find peaks at 1424.6, 1419.1, and 1414.0 Å, but we find prominent peaks at 1438.0, 1433.7, and 1431.0 Å. Taking into account the quantum defects and \(n^*\) values, the lowest autoionizing members listed in Table I correspond to \(n=8\) for both the strong and weak series. Since the occupied orbital in the ground state is \(5p\sigma_g^+\), the only Rydberg orbitals below the ionization potential which can be identified with the autoionizing series must involve \(n=6\) and 7. Based on the deduced quantum defects for the strong and weak series, the precursors for \(n=7\) should appear at \(\sim 1546\) Å (strong series) and \(\sim 1504\) Å (weak series). The closest band in the spectra reported by Donovan and Strachan has \(\lambda=1582.3,1578.5,\) and \(1574.8\) Å. Hence, no obvious correlation exists between the observations of Donovan and Strachan and the present work.

The gradual increase in the underlying continuum in Figs. 1 and 2 is due to formation of \(Sb^+\) in the \(2\Pi_u^+\) states. Wang et al.\(^5\) give \((8.5)\) eV as the adiabatic IP of \(Sb_2\). Dyke et al.\(^8\) deduce 8.36±0.10 eV, but the spectra they present are heavily contaminated by atomic Sb. We can immediately establish broad limits for this quantity, by noting the energy of the first observed autoionizing level (8.524 eV) of the strong series, and the precursor (unobserved) to the first autoionizing level of the weak series. If we take \(\delta_{p^r}\) =3.31 for the latter, then \(n^*=3.69\) and the unobserved level should occur at 8.25 eV. Therefore, 8.25 eV < adiabatic IP < 8.52 eV. There appears to be a distinct (unassigned) autoionizing level at 1464.4 Å = 8.467 eV, which reduces the upper limit accordingly. A still weaker feature appears at 1470.0 Å = 8.434 eV. Thus, the current experiments suggest 8.25 eV < adiabatic IP < 8.43 eV. The underlying continuum, which is a manifestation of a very broad Franck–Condon profile consequent upon removal of a bonding electron, appears to reach the background level at 1480–1485 Å = 8.38–8.35 eV. However, there may be a non-negligible contribution of hot bands. With an experimental temperature of \(\sim 1000\) K, and a vibrational frequency \(w_v(Sb_2)=270\) cm\(^{-1}\), the \(v''=1\) level is 2/3 as abundant as \(v''=0\), which makes it very difficult to disentangle a weak Franck–Condon tail from a Boltzmann tail.

If we accept \(IP(Sb_2)<8.43\) eV, then from the identity

\[
D_0(Sb_2^+)+IP(Sb_2)=D_0(Sb_2)+IP(Sb)
\]

we can deduce \(D_0(Sb_2)=D_0(Sb_2^+)+IP(Sb_2)+IP(Sb)\), which is \(\sim 8.43–8.608\) eV,\(^{12}\) or \(<-0.178\) eV. Thus, we come to the unexpected conclusion that removal of an electron from a bonding orbital increases the bond energy by more than 4 kcal/mol, although the internuclear distance increases and the vibrational frequency decreases.\(^{12}\) This has prompted us to examine the corresponding behavior of the other homonuclear pnictogen diatomic molecules. In \(N_2\), the ground state of \(N_2^+\) is \(\Sigma^+_g\), i.e., an electron is removed from the \(\sigma^+_g\) 2p orbital (also a bonding orbital) unlike the heavier pnictogens. Here, the bond energy of \(N_2^+\) is less than that of \(N_2\) by 23.8 kcal/mol, about as expected. For \(P_2,\ As_2,\) and \(Bi_2,\) \(D_0(Pn_2^+)-D_0(Pn_2)=-0.7,\ -2.3,\) and \(+1.2\) kcal/mol. To zeroth order, removal of an electron from the nominally bonding \(\pi\) orbital has almost no effect on the bond energy. In more detail, one sees a gradual increase in relative bonding between cation and neutral in the sequence \(P_2,\ As_2,\ Sb_2,\) and then a slight reversal for \(Bi_2\). The latter conclusions may be influenced slightly by more precise determinations of the molecular adiabatic ionization potentials, unencumbered by hot bands. However, the basic conclusion, \(D_0(Pn_2^+)=D_0(Pn_2)\) for \(Pn=P,\ As,\ Sb,\) and \(Bi\) seems clear.

We had recently noted\(^7\) that for the corresponding trimers, the atomization energy of the cation \([\Delta H_a(Pn_n^+)]\) is significantly greater than that of the neutral \([\Delta H_a(Pn_n)]\). The rationalization given for the trimers is that the cation has a closed shell structure, whereas the neutral species has one electron in the next higher orbital. In the present case, it is the cation which has an open shell.

The value for \(D_0(Sb_2)\) is fairly well known, but a more precise value would be desirable. The current value based on Knudsen cell mass spectrometric equilibria\(^6\) is 70.8 ± 1.5 kcal/mol = 3.07±0.07 eV. Sontag and Weber\(^7\) have observed vibrational levels of the ground state up to \(v''<60\). They have thereupon deduced \(D_0(Sb_2)=24,157\) \(\text{cm}^{-1}=2.995\) eV, presumably by some form of Birge–Sponer extrapolation. They also observed an excited \((K)\) state whose dissociation energy (from a linear Birge–Sponer extrapolation) is \(\leq 3706\) cm\(^{-1}\). If we assume (as tclay duc) that the asymptotic limits of the \(K\) state are \(5\Sigma^+_2+2D_{5/2}\), then (with the excitation of the \(K\) state given by them, and the \(4\Sigma^+_3--^2D_{3/2}\) excitation)\(^8\) we can deduce \(D_0(Sb_2)<25,219\) \(\text{cm}^{-1}=3.127\) eV. The present work could, in principle, have provided an alternative measurement, by examining the threshold for \(Sb^+\) from \(Sb_2\). It should occur at \(\sim 1059\) Å. Unfortunately, the intensity of our light source in this threshold region is weak, which results in a weak fragment signal and consequent statistical uncertainty.

B. \(Bi_2\)

The photoion yield curve of \(Bi_2^+\) (\(Bi_2\)), obtained by photoionization of the equilibrium vapor above heated bismuth metal, is shown in Fig. 3. The autoionizing structure between \(\sim 1570\) and \(1350\) Å was obtained with a wavelength resolution of 0.8 Å, the remainder with 2.5 Å resolution. Our spectrum bears only a vague resemblance to that of Saito et al.\(^6\) In Fig. 3, the curve rises monotonically from a threshold near 1700 Å = 7.3 eV. The spectrum of Saito et al. has an apparent onset at \(\sim 7.1\) eV, than manifests a weak, broad peak with maximum at \(\sim 7.4\) eV and a minimum at \(\sim 7.5\) eV. At higher energies, there is some correspondence—there is a peak at \(\sim 8.0\) eV, a minimum at \(\sim 8.2\) eV, and another peak maximum at \(\sim 8.3\) eV in both spectra. The spectrum in Fig. 3 appears qualitatively different from that of \(Sb_2\) and \(As_2\); a rather abrupt decline in intensity occurs beyond the last autoionizing peak.
which is not seen in the lighter homologs. The wavelengths of the peaks in the autoionizing region are listed in Table II.

As with Sb₂, one can formally describe the valence electronic configuration of Bi₂ as
\[
(\sigma_6s)^1(\sigma_6s)^1(\sigma_6p)^4, \quad X^1\Sigma^+_g (0^+_g)
\]
However, the influence of the spin–orbit effect is massive here. In the He I photoelectron spectrum of Wang et al., the \(^3\Pi_{3/2}\) and \(^3\Pi_{1/2}\) peaks created by ejection of an electron from the \(\pi_6p\) orbital are separated by 1.4 eV. Nevertheless, the \(^2\Sigma^+_g\) state formed by emission from the \(\sigma_6p\) orbital is still sharp in the photoelectron spectrum. As found earlier for As₂ and Sb₂, the autoionizing peaks appear to cluster into two series converging on the \(\pi_6p\) limit, i.e., \(^2\Sigma^+_g\). The precision is insufficient here to improve upon the ionization potential obtained by Wang et al. for this state, i.e., 9.307 ± 0.005 eV. The observed series are consistent with this limit, as can be seen from the effective quantum numbers \(n^*\) given in Table II. The derived \(\delta_{\text{pr}}\) and \(\delta_{\text{po}}\) quantum defects are 4.75 ± 0.05 and 4.33 ± 0.06, respectively. These values, and the corresponding ones for P₂, As₂, and Sb₂, are collected in Table III, and compared with the corresponding atomic values. The molecular \(\delta_{\text{po}}\) and \(\delta_{\text{pr}}\) typically straddle the atomic \(\delta_p\). In Bi₂, it appears as if the \(\text{pr} \) series, which starts out strong, becomes difficult to follow for higher members, and soon merges with the \(\text{po} \) series. By contrast, in As₂ and Sb₂, the stronger \(\text{po} \) series can be followed much further than the weaker \(\text{pr} \) series. This may be related to a change in coupling, perhaps connected with the large spin–orbit splitting in Bi₂.

The apparent adiabatic threshold is at \(\sim 1690 \, \text{Å} \equiv 7.34 \, \text{eV}\). This is somewhat lower than that reported in the photoelectron spectrum, 7.440 ± 0.007 eV.

C. The relationship between (\(\delta_{\text{pr}}-\delta_{\text{po}}\)) and the quadrupole moment

The difference \((\delta_{\text{pr}}-\delta_{\text{po}})\) is a measure of the departure from spherical symmetry of the electronic charge cloud of a molecule. Another measure of this asphericity is the quadrupole moment, \(Q\). It has been noted that the expression for the rate of rotational autoionization in two alternative theories contains a dependence on either \((\delta_{\text{pr}}-\delta_{\text{po}})\) or \(Q\).

Consider the interaction of a Rydberg electron with a molecular ion core. Buckingham has expressed this interaction in terms of an electrostatic energy, \(u_{\text{elec}}\), and an induction energy, \(u_{\text{ind}}\). If we neglect the Coulombic interaction, and (in this case) the charge–electric dipole interaction, then (in atomic units)
\[
u_{\text{elec}}=\frac{1}{2}Q_{zz}(r^{-3})n(3 \cos^2 \theta - 1)_{LL},
\]
and
\[
u_{\text{ind}}=\frac{1}{2}r^{-4}n(\alpha_\parallel + \alpha_\perp)(3 \cos^2 \theta - 1)_{LL},
\]
where \(Q_{zz}\) is the component of the electric quadrupole moment of the molecular ion core along the internuclear axis, \(\theta\) is the angle between the internuclear axis and the vector to the Rydberg electron, \(r\) is the distance from the molecular center to the Rydberg electron, \(\alpha\) is the polarizability of the molecular ion, \(\alpha_\parallel\) its parallel component (along the internuclear axis), and \(\alpha_\perp\) its perpendicular component.

It is clear from this expression that both \(u_{\text{elec}}\) and \(u_{\text{ind}}\) depend upon the \((n,l,\lambda)\) state of the Rydberg electron.

### Table II. Wavelengths and effective quantum numbers \((n^*)\) for autoionizing series in Bi₂.

<table>
<thead>
<tr>
<th>(\lambda, \text{Å} )</th>
<th>(n^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550±2*</td>
<td>3.225</td>
</tr>
<tr>
<td>1494±2</td>
<td>3.674</td>
</tr>
<tr>
<td>1451±2</td>
<td>4.225</td>
</tr>
<tr>
<td>1427±2</td>
<td>4.690</td>
</tr>
<tr>
<td>1405±2</td>
<td>5.310</td>
</tr>
<tr>
<td>1396±2</td>
<td>5.654</td>
</tr>
<tr>
<td>1381±2 (sh)</td>
<td>6.493</td>
</tr>
<tr>
<td>1368±3 (sh)*</td>
<td>7.470</td>
</tr>
</tbody>
</table>

*Based on IP (Bi₂) to \(^2\Sigma^+_g-9.307+0.005 \, \text{eV}\) from Ref 5.
*\(n_{\text{pr}}\) series member.
*\(n_{\text{po}}\) series member.
*Superposition of \(n_{\text{po}}\) and \(n_{\text{pr}}\) series members, (sh)—shoulder.

### Table III. Quantum defects in pnicogen atoms and diatomic molecules.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(\delta_{\text{po}})</th>
<th>(\delta_{\text{pr}})</th>
<th>(\delta_{\text{po}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.47±(1.4479)*</td>
<td>1.691±</td>
<td>1.497±</td>
</tr>
<tr>
<td>As</td>
<td>2.42–2.43±(2.4078)*</td>
<td>2.604±</td>
<td>2.172±</td>
</tr>
<tr>
<td>Sb</td>
<td>3.35±</td>
<td>3.672±0.028±</td>
<td>3.313±0.028±</td>
</tr>
<tr>
<td>Bi</td>
<td>4.45±</td>
<td>4.75±0.05±</td>
<td>4.33±0.06±</td>
</tr>
</tbody>
</table>

aReference 10.
bReference 9.
cReference 7.
dReference 29.
*Extrapolation of Ref. 9 from \(Z=50\) to \(Z=51\).
*Present results.
*From leading members, see the text for details.
*Extracted from energy levels given in Ref. 18; see also Ref. 4.
Jungen and Miescher have shown that the sum \( \mu_{\text{electron}} + \mu_{\text{ion}} = \Delta T_{n_{\text{I}}} \) represents the departure from pure hydrogenic behavior, i.e.,

\[
T_{n_{\text{I}}} = T_\omega - R/n^2 - \Delta T_{n_{\text{I}}}. 
\]

From the defining equation for the quantum defect \( \delta \),

\[
T_{n_{\text{I}}} = T_\omega - R/(n-k)^2 = T_\omega - R/(n^*)^2 
\]

one readily obtains

\[
\delta = n[1 - (1 + n^2\Delta T/R)^{-1/2}] 
\]

or alternatively,

\[
\delta = -n^*[1 - (1 - (n^*)^2\Delta T/R)^{-1/2}].
\]

The Buckingham expression for \( \Delta T \) can be made more explicit by substituting for \( \langle r^{-3} \rangle \), \( \langle r^{-4} \rangle \) and \( \langle 3 \cos^2 \theta - 1 \rangle \) of the Rydberg electron with hydrogenic values. Thus, \( \Delta T/R = -Q_{z_z} \), where \( l \) is the orbital angular momentum of the Rydberg electron, and \( \lambda \) its component along the internuclear axis.

The cumbersome expression simplifies for selected \( l \), \( \lambda \). Also, since \( \Delta T \) contains terms in \( 1/(n^*)^2 \) and \( 1/(n^*)^3 \), \( (n^*)^2\Delta T \) will have terms in \( 1/n^* \) and \( 1/(n^*)^2 \). Therefore, in the equation for \( \delta \), the term \( [1 - (n^*)^2\Delta T/R]^{-1/2} \) can be expanded, for large \( n^* \), yielding

\[
\delta(n) = A + B/(n^*) + C/(n^*)^2 + \cdots 
\]

Hemmerling, et al. have shown that for Rydberg series in \( \text{Li}_2 \) with \( l = 2, \lambda = 2 \) the result is

\[
\delta(n) = -0.088 - 0.0117/n - 1.14/n^2 + \cdots . 
\]

They note that the second term is small, and thus the Buckingham formula in this case leads to a Ritz-like equation for the Rydberg series, i.e., \( \delta(n) = A - C/n^2 \).

In the complete expression, \( \delta \) is a function of \( Q_{z_z} \), \( \alpha \) and \( \alpha_{q+} - \alpha_{q-} \). However, in the complete expression for \( \Delta T \), the term in \( \alpha \) is not multiplied by a term in \( \lambda \). Therefore, to zeroth order (i.e., the \( n \)-independent term), \( \delta(n) - \delta(n) \) is dependent on \( Q_{x_x} \) and \( \alpha_{q+} - \alpha_{q-} \), but not on \( \alpha \). The explicit expression for this leading term, for \( l = 1 - 4 \), is given as

\[
(\delta_{q+} - \delta_{q-}) = -Q_{z_x}/5 - (\alpha_{q+} - \alpha_{q-})/12.5, \quad l = 1 
\]

\[
= -Q_{z_x}/105 - (\alpha_{q+} - \alpha_{q-})/1102.5, \quad l = 2 
\]

\[
= -Q_{z_x}/630 - (\alpha_{q+} - \alpha_{q-})/14175, \quad l = 3 
\]

\[
= -Q_{z_x}/2310 - (\alpha_{q+} - \alpha_{q-})/88935, \quad l = 4. 
\]

Thus, for large \( n \), \( (\delta_{q+} - \delta_{q-}) \) becomes smaller in magnitude with increasing \( l \), and becomes more nearly proportional to \( Q_{x_x} \) alone. For the case of current interest \((l = 1)\),

\[
(\delta_{q+} - \delta_{q-}) \text{ becomes smaller in magnitude with increasing } l, \text{ and becomes more nearly proportional to } Q_{x_x} \text{ alone. For the case of current interest } (l = 1),
\]

the Buckingham equation is least likely to be applicable because of the well-known penetration effects of \( \rho \)-like orbitals. The term in \( (\alpha_{q+} - \alpha_{q-}) \) is comparable in magnitude to that in \( Q_{x_x} \), and the expansion in inverse powers of \( n \) (not given here explicitly) has convergence problems. However, \( (\alpha_{q+} - \alpha_{q-}) \) is itself a measure of asphericity. If its variation with pnictogen molecular size is similar to that of \( Q_{x_x} \), one can envisage this term as contributing to an effective \( Q_{x_x} \). Below, we proceed to test this hypothesis.

The polarizability \( \alpha \) is often considered as an approximately additive quantity. Thus, if \( \alpha(N) = 7.42 \) a.u.,\(^{26} \) one can estimate \( \alpha(N_2) = 14.84 \) a.u. The measured value of \( \alpha(N_2) \) is 11.744 a.u.,\(^{26} \) about 20% smaller. We shall apply this correction to the estimates of the other \( \alpha(Pn_2) \). The ratio \( (\alpha_{q+} - \alpha_{q-})/\alpha \) for \( N_2 \) is 0.394.\(^{27} \) Since \( \alpha - (\alpha_{q+} + 2\alpha_{q-})/3 \), we can determine the individual values of \( \alpha_{q+} \) and \( \alpha_{q-} \).

We wish to estimate \( (\alpha_{q+} - \alpha_{q-}) \) for \( Pn_2^+ \) with a \( 2^2\Sigma_g^+ \) core. The electron excited to a Rydberg orbit emanates from a \( \rho \)-orbital, which we estimate will reduce \( \alpha_{q+} \) to half its value. Thus, from the initially calculated \( \alpha_{q+} \) and \( \alpha_{q-} \), we obtain a value of \( (\alpha_{q+} - \alpha_{q-}) \) appropriate for \( Pn_2^+ \) \( (2^2\Sigma_g^+) \). As an illustration, \( \alpha(P) = 24.5 \) a.u.,\(^{26} \) one can estimate \( \alpha(P_2) = 0.8 \times 2\alpha(P) = 38.8 \) a.u., \( (\alpha_{q+} - \alpha_{q-}) \) \( \approx 0.394 \times 38.8 = 15.29 \) a.u., \( \alpha_{q+} = 48.99 \), \( \alpha_{q-} = 33.70 \) a.u., \( \alpha_{q+} \) (reduced) \( = 24.5 \) a.u., and the desired \( (\alpha_{q+} - \alpha_{q-}) \). Inserting this quantity into the expression for \( \delta_{q+} - \delta_{q-} \), and using our experimental value for \( \delta_{q+} - \delta_{q-} \), we deduce \( Q_{x_x} = 4.65 \) a.u. In Table IV, we list values for \( Q_{x_x} \) of the other pnictogen diatomic ions in the \( 2^2\Sigma_g^+ \) state calculated by the above procedure. Also shown are ab initio calculated values of \( Q_{x_x} \) for the same \( 2^2\Sigma_g^+ \) states of \( Pn_2^+ \) obtained by Krauss.\(^{28} \) Our estimated values of \( Q_{x_x} \), based on the experimental \( \delta_{q+} - \delta_{q-} \), the truncated Buckingham expression, and the approximated \( (\alpha_{q+} - \alpha_{q-}) \), have the same sign as the \( ab \) initio calculated values, but are uniformly lower. In the last column of Table IV, we list the corresponding ratios. The ratios average \( -0.64 \), and do not deviate greatly from this value. Hence, we conclude that the term in \( (\alpha_{q+} - \alpha_{q-}) \) roughly tracks the value of \( Q_{x_x} \).

### IV. CONCLUSIONS

In the photoion yield curves of \( \text{Sb}_2^+ \) (\( \text{Sb}_2 \)) and \( \text{Bi}_2^+ \) (\( \text{Bi}_2 \)), autoionizing structure is observed, which can be assigned to series converging upon the \( (\sigma_{\rho p})^{-1} 2^2\Sigma_g^+ \) state \((n = 5 \text{ for Sb, } n = 6 \text{ for Bi}) \). Two such series can be recognized in \( \text{Bi}_2 \), and at least two series for \( \text{Sb}_2 \). These are...
assigned as $np\sigma$ and $pnp\sigma$ Rydbergs, analogous to the cases of $P_2$ and $As_2$. An analysis of the series in $Sb_2$ leads to an improved value for the IP leading to formation of the $5p\sigma_e^{-1}2\Sigma_+^+$ state of 9.247 $\pm$ 0.003 eV. The adiabatic IP of $Sb_2$ is $< 8.43$ eV, and almost certainly $> 8.23$ eV. The adiabatic IP of $Bi_2$ is $\approx$ 7.34 eV.

The quantum defects $\delta_{pp}$ and $\delta_{po}$ are determined for these series in $Sb_2$ and $Bi_2$, and compared with earlier work on the analogous series in $P_2$ and $As_2$. The difference $(\delta_{pp} - \delta_{po})$, which is a measure of the departure from spherical symmetry, is related to the quadrupole moment of the molecular ion core. Sample calculations show that the experimental values of $(\alpha_{pp} - \alpha_{po})$ provide rough estimates for $Q_p$ of $Pn^+_2$ in the $A 2\Sigma_+^+$ state.

Upon excitation of electrons from the next deeper orbital, $\sigma_u ns$, window resonances were observed in $P_2$ ($n=3$) and $As_2$ ($n=4$). This, however, marked the presence of the sequences for $Sb_2$ ($n=5$) and $Bi_2$ ($n=6$). These expectations were supported by observations of window resonances in the atomic species $P$, $As$, and $Bi$, corresponding to excitation of electrons from the corresponding $ns$ orbital. (Data for $Sb$ in the relevant wavelength region are lacking.) Experimental difficulties have thus far prevented us from definitively establishing the presence of these window resonances for $Sb_2$ and $Bi_2$.

Although the uppermost occupied orbital in these pnictogen diatomic molecules is a bonding $pn$ orbital, an analysis leads to the surprising conclusion that $D_0(Pn^+_2) \geq D_0(Pn_2)$, although the internuclear distance increases and the vibrational frequency decreases upon ionization.

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13 The ionization potential of atomic phosphorus (10.48677 $\pm$ 0.00003 eV) is from W. C. Martin, J. Opt. Soc. Am. 49, 1071 (1959); the ionization potential of $P_2$ (10.516 eV) is from J. Berkowitz and B. Ruscic, in Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters, edited by C. Y. Ng (World Scientific, Singapore, 1991), pp. 36-38.
14 The ionization potential of atomic arsenic (9.7886 $\pm$ 0.0002 eV) is from K. S. Bhatia and W. E. Jones, Can. J. Phys. 49, 1773 (1971); that for $As_2$ (9.69 $\pm$ 0.02 eV) is from Ref. 1.
15 The ionization potential of atomic bismuth (7.28562 $\pm$ 0.00004 eV) is from W. A. Young, M. Y. Mirza, and W. W. Duley, J. Phys. B 13, 3175 (1980); for $Bi_2$ (7.336 eV) is obtained in the present work.
28 M. Krauss (private communication).