

Photoionization mass spectrometric studies of Sb₂ and Bi₂

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The photoion yield curves of Sb₂⁺ (Sb₂) and Bi₂⁺ (Bi₂) are presented. In both cases, two autoionizing series (designated *pσ* and *pπ*) are observed, converging on the excited ²Σ_g⁺ state. From this information, the ionization energy of the ²Σ_g⁺ state in Sb₂ is lowered to 9.247 eV. The difference in quantum defects, δ_{*pπ*} - δ_{*pσ*}, is shown to be related to the quadrupole moment of the molecular ion core of the ²Σ_g⁺ state in Pn₂⁺. The adiabatic ionization energies (AIP) are also decreased: AIP(Sb₂) < 8.43 eV, AIP(Bi₂) ≲ 7.34 eV. Although the uppermost occupied orbital is nominally a bonding *pπ* orbital, an analysis leads to the surprising conclusion that D₀(Pn₂⁺) ≳ D₀(Pn₂), where Pn = P, As, Sb, and Bi.

I. INTRODUCTION

We have recently reported on the vacuum ultraviolet photoionization spectra of As₂ and As₄.¹ In that paper, we demonstrated the presence of two regions in the spectrum of As₂ where autoionization was prominent—two series converging to the *A* ²Σ_g⁺ state of As₂⁺, and a window resonance series converging to the *B* ²Σ_u⁺ 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 4*sσ*_u orbital, has been correlated² with a window resonance series originating from the 4*s* orbital in atomic As. In fact, similar window resonance features have been observed² 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,³ and on atomic bismuth.⁴

The He I photoelectron spectra (PES) of Sb₂ and Bi₂ were obtained recently at relatively high resolution by Wang *et al.*⁵ 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.*,⁶ 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 temper-

ature 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 a 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.

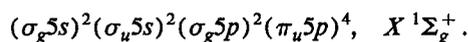
The saturated vapor above heated bismuth contains roughly comparable partial pressures of Bi and Bi₂, with Bi₃ and Bi₄ about two orders of magnitude less abundant. Hence, Bi₂ could be directly studied from such a source. However, antimony volatilizes almost entirely as tetramer. A satisfactory source 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



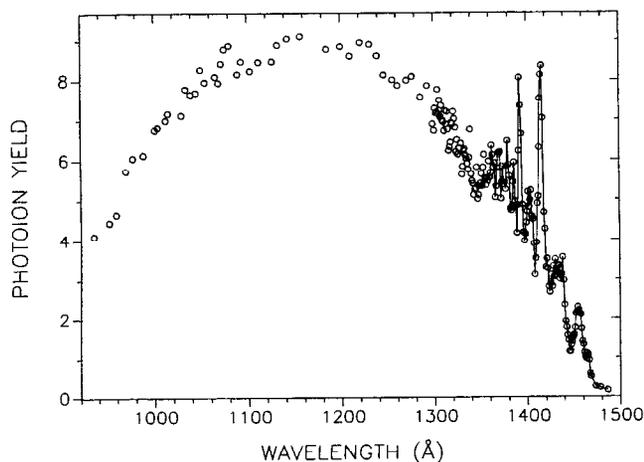
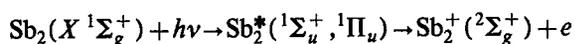


FIG. 1. The photoion yield curve of Sb_2^+ (Sb_2) between ~ 900 and 1500 Å obtained with a 2.5 Å (FWHM) bandwidth.

The He I photoelectron spectrum⁵ 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 $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$, respectively, and correspond to the spin-orbit pairs formed upon removal of a $\pi_u 5p$ electron. The sharp peak, at 9.275(5) eV, is assigned to $^2\Sigma_g^+$, formed upon removal of an electron from the $\sigma_g 5p$ 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 $^2\Sigma_g^+$ limit, analogous to the pattern observed in P_2 and As_2 . The electric dipole selection rules for the transition



require that the outgoing electron be odd (p , f , etc). If Sb_2^* is described by a $^2\Sigma_g^+$ core, then the Rydberg electron must also be odd. For As_2 , Carroll and Mitchell⁷ has as-

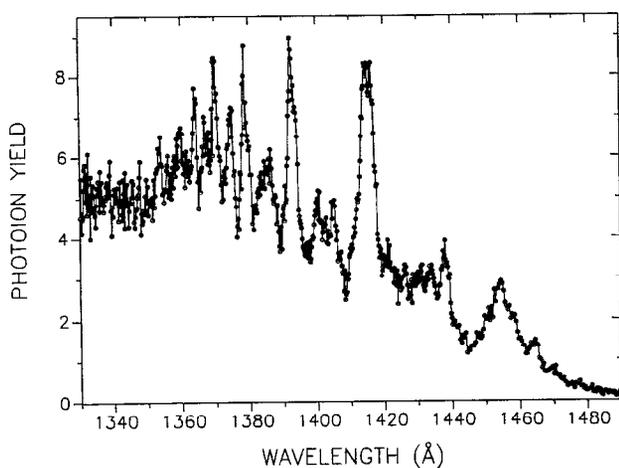


FIG. 2. A higher resolution (0.83 Å FWHM bandwidth) photoion yield curve of Sb_2^+ (Sb_2), revealing fine structure in the autoionizing series between 1330 and 1490 Å.

TABLE I. Wavelengths and effective quantum numbers (n^*) for autoionizing series in Sb_2 . (A) Strong series and (B) weak series.

λ , Å	n^* (IP=9.275 eV)	n^* (IP=9.260 eV)	n^* (IP=9.247 eV)
(A)			
1454.6 ± 0.4	4.255	4.298	4.337
1415.0 ± 1.0	5.151	5.227	5.297
1392.2 ± 0.4	6.069	6.199	6.313
1378.6 ± 0.4	6.952	7.145	7.326
1369.8 ± 0.4	7.798	8.074	8.337
1363.8 ± 0.4	8.601	8.975	9.341
1359.5 ± 0.5	9.364	9.852	10.344
(B)			
1438.0 ± 0.4	4.565	4.618	4.666
1405.2 ± 0.4	5.488	5.581	5.666
1386.2 ± 0.4	6.413	6.564	6.703
1374.8 ± 0.4	7.281	7.504	7.713
1367.0 ± 0.4	8.143	8.458	8.763

signed 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 (f 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 $^2\Sigma_g^+$, 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 λ , 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 $\delta = 3.672 \pm 0.028$. 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 $\delta_{p\pi}$ and $\delta_{p\sigma}$ appear to straddle the atomic δ_p , although in this case $\delta_{p\pi}$ seems to be closer to δ_p .

Donovan and Strachan¹¹ have reported the observation of absorption bands in the vacuum ultraviolet attributed to Sb_2 . By assuming quantum defects, they have deduced an IP(Sb_2) ~ 9.3 eV, which they believed to be the first ionization potential, corresponding to $(p\pi_u)^{-1}$. It is very close

to our deduced higher ionization potential, $(p\sigma_g)^{-1}$. Hence, one might expect to see some relation between the absorption series observed by Donovan and Strachan and the autoionizing members converging to $(p\sigma_g)^{-1}$ reported here. One region (~ 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 ~ 1546 Å (strong series) and ~ 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_2^+ 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 $\delta_{pr} = 3.31$ for the latter, then $n^* = 3.69$ and the unobserved level should occur at 8.25 eV. Therefore, $8.25 \text{ eV} < \text{adiabatic IP} < 8.52 \text{ eV}$. There appears to be a distinct (unassigned) autoionizing level at $1464.4 \text{ Å} \equiv 8.467 \text{ eV}$, which reduces the upper limit accordingly. A still weaker feature appears at $1470.0 \text{ Å} \equiv 8.434 \text{ eV}$. Thus, the current experiments suggest $8.25 \text{ eV} < \text{adiabatic IP} < 8.43 \text{ eV}$. 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 $1480\text{--}1485 \text{ Å} \equiv 8.38\text{--}8.35 \text{ eV}$. However, there may be a non-negligible contribution of hot bands. With an experimental temperature of ~ 1000 K, and a vibrational frequency $w_e(\text{Sb}_2) = 270 \text{ cm}^{-1}$, 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 $\text{IP}(\text{Sb}_2) < 8.43 \text{ eV}$, then from the identity

$$D_0(\text{Sb}_2^+) + \text{IP}(\text{Sb}_2) = D_0(\text{Sb}_2) + \text{IP}(\text{Sb})$$

we can deduce $D_0(\text{Sb}_2) - D_0(\text{Sb}_2^+) = \text{IP}(\text{Sb}_2) - \text{IP}(\text{Sb})$, which is $< 8.43 - 8.608 \text{ eV}$,¹² or $< -0.178 \text{ eV}$. 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 $^2\Sigma_g^+$, 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 ,¹³ As_2 ,¹⁴ and Bi_2 ,¹⁵ $D_0(\text{Pn}_2) - D_0(\text{Pn}_2^+) = 0.7$, -2.3 , and $+1.2$ kcal/mol. To zeroth order, removal of an electron from the nominally bonding π_u 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, $D_0(\text{Pn}_2^+) \gtrsim D_0(\text{Pn}_2)$ for $\text{Pn} = \text{P}$, As , Sb , and Bi seems clear.

We had recently noted³ that for the corresponding trimers, the atomization energy of the cation [$\Delta H_{\text{at}}(\text{Pn}_3^+)$] is significantly greater than that of the neutral [$\Delta H_{\text{at}}(\text{Pn}_3)$]. 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 $D_0(\text{Sb}_2)$ is fairly well known, but a more precise value would be desirable. The current value based on Knudsen cell mass spectrometric equilibria¹⁶ is $70.8 \pm 1.5 \text{ kcal/mol} \equiv 3.07 \pm 0.07 \text{ eV}$. Sontag and Weber¹⁷ have observed vibrational levels of the ground state up to $v'' \leq 60$. They have thereupon deduced $D_0(\text{Sb}_2) = 24,157 \text{ cm}^{-1} \equiv 2.995 \text{ eV}$, 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 $\lesssim 3706 \text{ cm}^{-1}$. If we assume (as they do) that the asymptotic limits of the K state are $^4S_{3/2} + ^2D_{5/2}$, then (with the excitation of the K state given by them, and the $^4S_{3/2} \rightarrow ^2D_{5/2}$ excitation)¹⁸ we can deduce $D_0(\text{Sb}_2) < 25,219 \text{ cm}^{-1} \equiv 3.127 \text{ eV}$. The present work could, in principle, have provided an alternative measurement, by examining the threshold for Sb^+ from Sb_2 . It should occur at ~ 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. Bi₂

The photoion yield curve of $\text{Bi}_2^+(\text{Bi}_2)$, obtained by photoionization of the equilibrium vapor above heated bismuth metal, is shown in Fig. 3. The autoionizing structure between ~ 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 $1700 \text{ Å} \equiv 7.3 \text{ eV}$. The spectrum of Saito *et al.* has an apparent onset at $\sim 7.1 \text{ eV}$, than manifests a weak, broad peak with maximum at $\sim 7.4 \text{ eV}$ and a minimum at 7.5 eV . At higher energies, there is some correspondence—there is a peak at $\sim 8.0 \text{ eV}$, a minimum at $\sim 8.2 \text{ eV}$, and another peak maximum at $\sim 8.3 \text{ eV}$ 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,

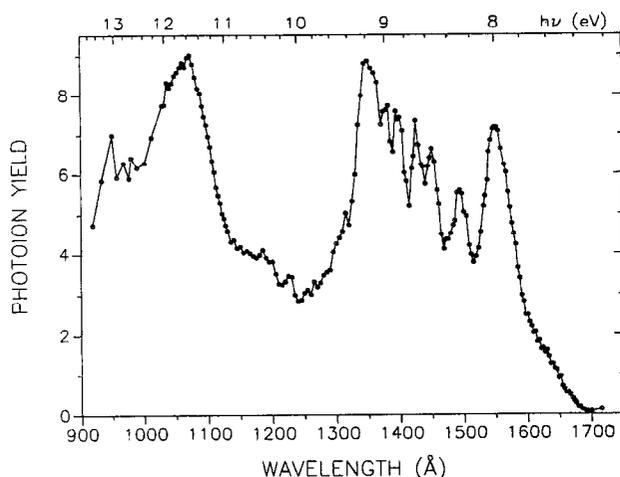


FIG. 3. The photoion yield curve of Bi₂⁺ (Bi₂). In the region of autoionizing structure (~1570–1350 Å) the bandwidth is 0.83 Å (FWHM); to shorter wavelength, it is 2.5 Å.

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

$$(\sigma_g 6s)^2 (\sigma_u 6s)^2 (\sigma_g 6p)^2 (\pi_u 6p)^4, \quad X^1 \Sigma_g^+ (0_g^+)$$

However, the influence of the spin-orbit effect is massive here. In the He I photoelectron spectrum of Wang *et al.*,⁵ the ²Π_{u,3/2} and ²Π_{u,1/2} peaks created by ejection of an electron from the π_u6p orbital are separated by 1.4 eV. Nevertheless, the ²Σ_g⁺ state formed by emission from the σ_g6p 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 (σ_g6p)⁻¹ limit, i.e., ²Σ_g⁺. The precision is insufficient here to improve upon the ionization potential obtained by Wang *et al.*⁵ 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 δ_{pσ} and δ_{pπ} quantum defects are 4.75 ± 0.05 and 4.33 ± 0.06, respectively. These values, and the corresponding ones for

TABLE II. Wavelengths and effective quantum numbers (*n*^{*}) for autoionizing series in Bi₂.

λ, Å	<i>n</i> [*]
1550 ± 2 ^b	3.225
1494 ± 2 ^c	3.674
1451 ± 2 ^b	4.225
1427 ± 2 ^c	4.690
1405 ± 2 ^b	5.310
1396 ± 2 ^c	5.564
1380 ± 2 ^d	6.493
1368 ± 3 (sh) ^d	7.470

^aBased on IP (Bi₂) to ²Σ_g⁺ = 9.307 ± 0.005 eV from Ref. 5.

^b*npσ* series member.

^c*npπ* series member.

^dSuperposition of *npσ* and *npπ* series members, (sh)—shoulder.

TABLE III. Quantum defects in pnictogen atoms and diatomic molecules.

	Atom δ _p	Molecule	
		δ _{pσ}	δ _{pπ}
P	1.47 ^a (1.4479) ^b	1.691 ^c	1.497 ^c
As	2.42–2.43 ^d (2.4078) ^b	2.604 ^c	2.172 ^c
Sb	~3.35 ^f	3.672 ± 0.028 ^g	3.313 ± 0.028 ^{g,h}
Bi	~4.45 ^k	4.75 ± 0.05 ^g	4.33 ± 0.06 ^g

^aReference 10.

^bReference 9.

^cReference 7.

^dReference 29.

^eExtrapolation of Ref. 9 from Z=50 to Z=51.

^fPresent results.

^gFrom leading members, see the text for details.

^hExtracted from energy levels given in Ref. 18; see also Ref. 4.

P₂, As₂, and Sb₂, are collected in Table III, and compared with the corresponding atomic values. The molecular δ_{pσ} and δ_{pπ} typically straddle the atomic δ_p. In Bi₂, it appears as if the pσ series, which starts out strong, becomes difficult to follow for higher members, and soon merges with the pπ series. By contrast, in As₂ and Sb₂, the stronger pσ series can be followed much further than the weaker pπ 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 ~1690 Å ≡ 7.34 eV. This is somewhat lower than that reported in the photoelectron spectrum, 7.440 ± 0.007 eV.

C. The relationship between (δ_{pπ} - δ_{pσ}) and the quadrupole moment

The difference (δ_{pπ} - δ_{pσ}) 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 noted¹⁹ that the expression for the rate of rotational autoionization in two alternative theories contains a dependence on either (δ_{pπ} - δ_{pσ}) or *Q*.

Consider the interaction of a Rydberg electron with a molecular ion core. Buckingham²⁰ has expressed this interaction in terms of an electrostatic energy, *u*_{elec}, and an induction energy, *u*_{ind}. If we neglect the Coulombic interaction, and (in this case) the charge-electric dipole interaction, then (in atomic units)

$$u_{\text{elec}} = \frac{1}{2} Q_{zz} \langle r^{-3} \rangle_{n,l} \langle 3 \cos^2 \theta - 1 \rangle_{l,\lambda}$$

and

$$u_{\text{ind}} = \frac{1}{2} \langle r^{-4} \rangle_{n,l} [\alpha_{\parallel} + \frac{1}{3} (\alpha_{\parallel} - \alpha_{\perp}) \langle 3 \cos^2 \theta - 1 \rangle_{l,\lambda}],$$

where *Q*_{zz} is the component of the electric quadrupole moment of the molecular ion core along the internuclear axis, θ 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, α is the polarizability of the molecular ion, α_∥ its parallel component (along the internuclear axis), and α_⊥ its perpendicular component.

It is clear from this expression that both *u*_{elec} and *u*_{ind} depend upon the (*n*, *l*, λ) state of the Rydberg electron.

Jungen and Miescher²¹ have shown that the sum $u_{\text{elec}} + u_{\text{ind}} = \Delta T_{n,l,\lambda}$ represents the departure from pure hydrogenic behavior, i.e.,

$$T_{n,l,\lambda} = T_{\infty} - R/n^2 - \Delta T_{n,l,\lambda}.$$

From the defining equation for the quantum defect δ ,

$$T_{n,l,\lambda} = T_{\infty} - R/(n - \delta)^2 = T_{\infty} - R/(n^*)^2$$

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 ΔT 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.^{22,23} Thus,

$$\begin{aligned} \Delta T/R = & \frac{-Q_{zz}}{(n^*)^3(l+1)(l+1/2)l} \frac{3\lambda^2 - l(l+1)}{l(2l-1)} \frac{2l}{(2l+3)} \\ & + \frac{3(n^*)^2 - l(l+1)}{2(n^*)^5(l+3/2)(l+1)(l+1/2)l(l-1/2)} \\ & \times \left(\alpha - \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp}) \frac{3\lambda^2 - l(l+1)}{l(2l-1)} \cdot \frac{2l}{(2l+3)} \right), \end{aligned}$$

where l is the orbital angular momentum of the Rydberg electron, and λ its component along the internuclear axis.

This cumbersome expression simplifies for selected l , λ . Also, since ΔT contains terms in $1/(n^*)^3$ and $1/(n^*)^5$, $(n^*)^2 \Delta T$ will have terms in $1/n^*$ and $1/(n^*)^3$. Therefore, in the equation for δ , the term $[1 - (n^*)^2 \Delta T/R]^{1/2}$ can be expanded, for large n^* , yielding

$$\delta(n^*) = A + B/(n^*) + C/(n^*)^2 + \dots$$

Hemmerling, *et al.*²⁴ have shown that for Rydberg series in Li₂ with $l=2$, $\lambda=2$ the result is

$$\delta(n) = -0.088 - 0.0117/n - 1.14/n^2 + \dots$$

They note that the second term is small, and thus the Buckingham formula in this case leads to a Ritz-like²⁵ equation for the Rydberg series, i.e., $\delta(n) = A - C/n^2$.

In the complete expression, δ is a function of Q_{zz} , α and $(\alpha_{\parallel} - \alpha_{\perp})$. However, in the complete expression for ΔT , the term in α is not multiplied by a term in λ . Therefore, to zeroth order (i.e., the n -independent term), $(\delta_{\pi} - \delta_{\sigma})$ is dependent on Q_{zz} and $(\alpha_{\parallel} - \alpha_{\perp})$, but not on α . The explicit expression for this leading term, for $l=1-4$, is given as

$$\begin{aligned} (\delta_{\pi} - \delta_{\sigma}) = & -Q_{zz}/5 - (\alpha_{\parallel} - \alpha_{\perp})/12.5, \quad l=1 \\ = & -Q_{zz}/105 - (\alpha_{\parallel} - \alpha_{\perp})/1102.5, \quad l=2 \\ = & -Q_{zz}/630 - (\alpha_{\parallel} - \alpha_{\perp})/14,175, \quad l=3 \\ = & -Q_{zz}/2310 - (\alpha_{\parallel} - \alpha_{\perp})/88,935, \quad l=4. \end{aligned}$$

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

TABLE IV. Quadrupole moments Q_{zz} of Pn_2^+ in the $A^2\Sigma_g^+$ state as determined from $(\delta_{p\pi} - \delta_{p\sigma})$ and estimated $(\alpha_{\parallel} - \alpha_{\perp})$ compared with *ab initio* values.

Pn_2^+	Q_{zz}^a	Q_{zz}^b	Q_{zz}^a/Q_{zz}^b
P_2^+	4.65	7.20	0.646
As_2^+	6.53	10.02	0.652
Sb_2^+	>8.48	13.87	>0.611
Bi_2^+	9.60	15.49	0.620

^aCalculated from experimental $(\delta_{p\pi} - \delta_{p\sigma})$ and estimated values of $(\alpha_{\parallel} - \alpha_{\perp})$, see the text.

^b*Ab initio* values from M. Krauss (Ref. 28).

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

The polarizability α is often considered as an approximately additive quantity. Thus, if $\alpha(\text{N}) = 7.42$ a.u.,²⁶ one can estimate $\alpha(\text{N}_2) = 14.84$ a.u. The measured value of $\alpha(\text{N}_2)$ is 11.744 a.u.,²⁶ about 20% smaller. We shall apply this correction to the estimates of the other $\alpha(\text{Pn}_2)$. The ratio $(\alpha_{\parallel} - \alpha_{\perp})/\alpha$ for N_2 is 0.394.²⁷ Since $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$, we can determine the individual values of α_{\parallel} and α_{\perp} .

We wish to estimate $(\alpha_{\parallel} - \alpha_{\perp})$ for Pn_2^+ with a $2\Sigma_g^+$ core. The electron excited to a Rydberg orbit emanates from a $p\sigma$ orbital, which we estimate will reduce α_{\parallel} to half its value. Thus, from the initially calculated α_{\parallel} and α_{\perp} , we obtain a value of $(\alpha_{\parallel} - \alpha_{\perp})$ appropriate for Pn_2^+ ($2\Sigma_g^+$). As an illustration, $\alpha(\text{P}) = 24.5$ a.u., $\alpha(\text{P}_2) \cong 0.8 \times 2\alpha(\text{P}) \cong 38.8$ a.u., $(\alpha_{\parallel} - \alpha_{\perp}) \text{P}_2 \cong 0.394 \times 38.8 = 15.29$ a.u., $\alpha_{\parallel} = 48.99$ a.u., $\alpha_{\perp} = 33.70$ a.u., α_{\parallel} (reduced) = 24.5 a.u., and the desired $(\alpha_{\parallel} - \alpha_{\perp})$, P_2^+ , $2\Sigma_g^+ \cong -9.20$ a.u. Inserting this quantity into the expression for $\delta_{p\pi} - \delta_{p\sigma}$, and using our experimental value for $\delta_{p\pi} - \delta_{p\sigma}$, we deduce $Q_{zz} \cong 4.65$ a.u. In Table IV, we list values for Q_{zz} of the other pnictogen diatomic ions in the $2\Sigma_g^+$ state calculated by the above procedure. Also shown are *ab initio* calculated values of Q_{zz} for the same $2\Sigma_g^+$ states of Pn_2^+ obtained by Krauss.²⁸ Our estimated values of Q_{zz} , based on the experimental $(\delta_{p\pi} - \delta_{p\sigma})$, the truncated Buckingham expression, and the approximated $(\alpha_{\parallel} - \alpha_{\perp})$, 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 $(\alpha_{\parallel} - \alpha_{\perp})$ roughly tracks the value of Q_{zz} .

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 $(\sigma_g n p)^{-1}$, $2\Sigma_g^+$ state ($n=5$ for Sb, $n=6$ for Bi). Two such series can be recognized in Bi_2 , and at least two series for Sb_2 . These are

assigned as $np\pi$ and $np\sigma$ Rydbergs, analogous to the cases of P₂ and As₂. An analysis of the series in Sb₂ leads to an improved value for the IP leading to formation of the $5p\sigma_g^{-1}, 2\Sigma_g^+$ state of 9.247 ± 0.003 eV. The adiabatic IP of Sb₂ is < 8.43 eV, and almost certainly > 8.23 eV. The adiabatic IP of Bi₂ is ~ 7.34 eV.

The quantum defects $\delta_{p\pi}$ and $\delta_{p\sigma}$ are determined for these series in Sb₂ and Bi₂, and compared with earlier work on the analogous series in P₂ and As₂. The difference ($\delta_{p\pi} - \delta_{p\sigma}$), 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 ($\delta_{p\pi} - \delta_{p\sigma}$) and estimates of ($\alpha_{\parallel} - \alpha_{\perp}$) provide rough estimates for Q_{zz} of Pn₂⁺ in the $A^2\Sigma_g^+$ state.

Upon excitation of electrons from the next deeper orbital, $\sigma_{u,n}$ s, window resonances were observed in P₂ ($n=3$) and As₂ ($n=4$). On this basis, window resonances were also anticipated for Sb₂ ($n=5$) and Bi₂ ($n=6$). These expectations were supported by observations of window resonances in the atomic species P,¹⁰ As,²⁹ and Bi,⁴ 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 Sb₂ and Bi₂.

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

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