Photoelectron spectroscopy and electronic structure of clusters of the group V elements. II. Tetramers: Strong Jahn–Teller coupling in the tetrahedral $^2E$ ground states of P$_4^+$, As$_4^+$, and Sb$_4^+$

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High resolution HeI (584 Å) photoelectron spectra have been obtained for the tetrameric clusters of the group V elements: P$_4^+$, As$_4^+$, and Sb$_4$.$^*$ The spectra establish that the ground $^2E$ states of tetrahedral P$_4^+$, As$_4^+$, and Sb$_4^+$ are unstable with respect to distortion in the $v_3$ (e) vibrational coordinate. The $E\otimes e$ Jahn–Teller problem has been treated in detail, yielding simulated spectra to compare with experimental ones. Vibronic calculations, extended to second order (quadratic coupling) for P$_4^+$, account for vibrational structure which is partially resolved in its photoelectron spectrum. A Jahn–Teller stabilization energy of 0.65 eV is derived for P$_4^+$, which can be characterized in its ground vibronic state as being highly distorted, and highly fluxional. Linear-only Jahn–Teller coupling calculations performed for As$_4^+$ and Sb$_4^+$, show good qualitative agreement with experimental spectra, yielding stabilization energies of 0.84 and 1.4 eV, respectively.

I. INTRODUCTION

Elemental clusters fulfill a central role in contemporary chemistry as an important bridge between molecules and condensed matter. Increasingly, the focus of effort in cluster science is turning to questions concerned with the structural and dynamical properties of isolated clusters, and the relation of those properties to cluster reactivity.$^1$ This is a challenging problem, owing to the often complex vibrational and electronic structure of elemental clusters. Available spectroscopic methods fall short when applied to polydispersed clusters from supersonic expansions, and, outside of a few dimers and a handful of trimers, few data exist on the vibrational frequencies and electronic energy levels of neutral elemental clusters. The situation is a little better for charged clusters. For direct spectroscopy, size selection can be achieved by mass filtering, and information on the energy levels of cations can be obtained in transitions from neutrals by photoelectron spectroscopy, in some cases with accompanying confirmation of parent mass.$^2$ Much of this work has focused on transition metals. Main group elements also form interesting and important clusters. In particular, the elements of group V have long been known to form molecularly bound clusters, especially tetrahedral tetramers.$^3$ We have exploited the naturally high concentration of such species in supersonic expansions of the group V elements from high temperature molecular beam source to obtain structural details on the geometries and energy levels of the corresponding cations. In part I of our investigation,$^4$ we reported on the high resolution photoelectron spectroscopy of the dimers: As$_2$, Sb$_2$, and Bi$_2$. In the current paper, we turn our attention to the tetrameric systems: P$_4$, As$_4$, and Sb$_4$.

Among the polyatomic clusters, only Cu$_3$$^5$, Na$_5$$^6$, Al$_7$$^7$, A$_5$$^8$, and Li$_3$$^9$ have thus far been spectroscopically well characterized. Interestingly, spectroscopic data for all of these trimers establish that Jahn–Teller effects play an important role in determining ground state properties. In each case, the trimers in $D_{3h}$ symmetry have a $^2E$ ground state, which couples with the doubly degenerate $v_3$ (e) vibrational mode. Symmetric geometries are envisioned for higher clusters, and Jahn–Teller effects may well extend to such systems.

The tetramers of P, As, and Sb have $T_d$ symmetry with a $^1A_g$ ground state. In $T_d$ symmetry, molecular orbital calculations show that the ground state term of the tetrameric cations is $^2E$, while that of their first excited states is $^2T_2$.$^{10}$ Both these states, being orbitally degenerate, are subject to Jahn–Teller distortions. Thus, these species can be viewed as prototypes for studying the Jahn–Teller effect in larger metal clusters with $T_d$ symmetry.

Lower resolution HeI photoelectron spectra of P$_4$$^{11}$ As$_4$$^{12}$, and Sb$_4$$^{13,14}$ have been reported. Except for the $^1A_g$ state of P$_4^+$, no vibrational resolution has been achieved. Hence, little is known about the spectroscopy of the cationic states of these simple cluster species. A few electronic structure calculations exist for the neutral clusters, P$_4$$^{10,15}$ As$_4$$^{15a,16}$, and Sb$_4$$^{14}$ But as yet none have been carried out for the ionic states.

We have obtained high resolution photoelectron spectra for all three cluster species. Vibrational structure is completely resolved for the $^1A_g$ states of P$_4^+$ and As$_4^+$, while that in the Jahn–Teller active $^2E$ and $^2T_2$ states is only partially resolved due to smaller vibrational frequencies. Strong Jahn–Teller distortions are found in the $^2E$ states, owing to coupling in the $v_3$ vibrational coordinate, in each case splitting the spectra into two broad bands. In the current paper, we focus on the ground $^2E$ states. The $E\otimes e$ Jahn–Teller
problem is explored in detail for the $^2E$ states of these tetrameric cations, representing the first vibronic studies for $T_d$ clusters. The $^2T_2$ and $^2A_1$ states will be discussed in a subsequent paper.

The rest of the paper is organized as follows. In Sec. II, we briefly present the experimental procedure. The results are presented in Sec. III. The discussion and the comparisons of the vibronic calculations with the experimental results are given in Sec. IV. The conclusions appear in Sec. V.

II. EXPERIMENT

The high temperature molecular beam source used in the current experiments has been described in detail previously. The experimental conditions related to the current experiments are given collectively in Table I. As pointed out previously, evaporation of pure phosphorus and arsenic give essentially neat tetramer species. Pure elements are used for all three cases. Phosphorus has three allotropes; forms, white, red, and black. The white form is highly reactive even at room temperature and difficult to handle. So, the more stable red form is used. Antimony is less volatile, and a higher temperature is required for the experiment. At the experimental temperature given in Table I, the vapor of antimony contains three species: atoms, dimers, and tetramers. As a result, the photoelectron spectrum is a mixture of the three. All samples (99% purity) were purchased from CERAC and used directly.

The details of the photoelectron spectrometer have also been described previously. Argon and xenon are used as calibration gases. The energy resolution is 12 meV, as measured with the $^2P_{3/2}$ photoelectrons. To avoid drift of the energy scale under high temperature conditions, we have kept each photoelectron scan under 1 h. Multiple scans have been taken and added together to increase counting statistics. The effective energy resolution on the final spectrum is about 15 meV.

III. RESULTS

The photoelectron spectra of $P_4$, $As_4$, and $Sb_4$ are shown in Figs. 1–3, respectively. The three clusters are isoelectronic and all have the same tetrahedral geometry. Thus, their photoelectron spectra are very similar, with the $P_4^+$ and $As_4^+$ spectra showing vibrational resolution. Under $T_d$ symmetry, the valence electronic configuration of these clusters can be written as

![Image of Fig. 1](https://via.placeholder.com/150)

**FIG. 1.** The HeI photoelectron spectrum of $P_4^+$. HB indicates a hot band transition.

![Image of Fig. 2](https://via.placeholder.com/150)

**FIG. 2.** The HeI photoelectron spectrum of $As_4^+$. HB indicates hot band transitions.

![Image of Fig. 3](https://via.placeholder.com/150)

**FIG. 3.** The HeI photoelectron spectrum of $Sb_4^+$. The arrow indicates the $^2Σ_g^+$ band of $Sb_4^+$. Some contributions from $Sb^+$ atomic lines are subtracted. The $^2Σ_g^+$ bands have some contributions from the $^2Π_{1/2}$ and $^2Π_{3/2}$ bands of $Sb^+$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (Torr)</th>
<th>$\phi$ (mm)</th>
<th>Starting materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_4$</td>
<td>620</td>
<td>500 (He)</td>
<td>0.16</td>
</tr>
<tr>
<td>$As_4$</td>
<td>650</td>
<td>200 (He)</td>
<td>0.16</td>
</tr>
<tr>
<td>$Sb_4$</td>
<td>1150</td>
<td>600 (Ne)</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*Oven temperature (+50 K).

*Carrier gas pressure.

*Nozzle diameter.

*Samples purchased from CERAC.
where the 1a_{1} and 1t_{2} MOs are mainly of the valence atomic s orbital character, and the 2a_{1}, 2t_{2}, and 1e MOs of the valence p character. As pointed out previously, the atomic ionization cross sections of the ns orbitals are two to three orders of magnitude smaller than the np orbitals at the HeI photon energy (21.218). Consequently, the 1a_{1} and 1t_{2} MOs also have very small ionization cross sections. Thus, only the ionizations of the outermost three MOs are observed, as indicated in Figs. 1–3. The Sb_{2}^{+} spectrum has a contribution from the Sb_{2} species, as noted in Fig. 3. The 2\Pi_{u} bands of Sb_{2}^{+} overlap exactly with the (2t_{2})^{-1} bands of Sb_{2}^{+}, though the contribution from the 2\Pi_{u} bands of Sb_{2}^{+} is expected to be small. Both the small vibrational frequencies and the poor statistics in the Sb_{2}^{+} spectrum are responsible for the lack of vibrational structure, particularly in the (2a_{1})^{-1} band.

With T_{d} symmetry, these three clusters have 1A_{1} ground states. Removal of an electron from the 1e or 2t_{2} MOs creates 2E and 2T_{2} final states in the ions, respectively. The 2E state is orbitally doubly degenerate and the 2T_{2} state triply degenerate. According to the Jahn–Teller theorem, these two states are Jahn–Teller active and the tetrahedral geometries of the molecular ions are unstable in these two states against asymmetric vibrations. The 2A_{1} excited states of the molecular ions from (2a_{1})^{-1} are not orbitally degenerate and should maintain the T_{d} symmetry.

The six normal modes of vibrations for a tetrahedral M_{4} molecule are shown in Fig. 4. The \nu_{e} (e) mode is doubly degenerate and the \nu_{3} (t_{2}) mode is triply degenerate. The vibrational frequencies for P_{4}, As_{4}, and Sb_{4} are given in Table II. The \nu_{1} (a_{1}) mode is totally symmetric and cannot distort the T_{d} symmetry. However, the \nu_{2} and \nu_{3} modes are both Jahn–Teller active. From group theory, only the \nu_{2} mode can be Jahn–Teller active in the 2E state while both the \nu_{2} and \nu_{3} modes can be coupled in the 2T_{2} state. In the present paper, we focus on a full analysis of the vibronic structure observed in each case for the 2E cation ground states. In the following paper, we consider more qualitative aspects of the structure of excited state bands, as well as overall trends in ionization potential.

It can be seen from Figs. 1–3 that two photoelectron bands are observed for ionization of the 1e orbital as a result of the Jahn–Teller coupling with the \nu_{2} vibrations (see below). Because of the strong Jahn–Teller effect, adiabatic IPs to the ground 2E states cannot be obtained by direct inspection, and only upper limits can be estimated from the experimental photoelectron spectra. Vibronic calculations yield better values for the adiabatic IPs.

IV. DISCUSSION: THE JAHN–TELLER EFFECT AND VIBRONIC STRUCTURE IN THE 2E GROUND STATES OF T_{d} GROUP V CATION TETRAMERS

A. Potential energy surfaces

The prominent two-peaked spectral intensity distributions evident to a remarkably similar degree in the (1e)\rightarrow{1} bands of all three tetramers signal strong Jahn–Teller distortions differentiating the molecular ion ground states from the highly symmetric tetrahedral configurations of the corresponding neutrals. As noted above, the 2E (G_{5/2}) terms associated with these 1e-orbital vacancies are, in each case, subject to Jahn–Teller vibronic coupling in the \nu_{2} (e) normal coordinate. This coupling displaces stable molecular configurations from high symmetry, and, as a consequence, distributes spectral intensity over progressions of vibronically excited bands. A qualitative understanding of this effect can be achieved by examining the adiabatic potential energy surfaces of the Jahn–Teller active system in classical terms.

Let \psi_{+} denote the complex electronic wave functions of the doubly degenerate electronic term, and H_{e}(Q_{e}) the electronic Hamiltonian at the undistorted nuclear configuration. Surfaces of the single-mode E \otimes e Jahn–Teller problem are obtained most simply by diagonalizing the electronic Hamiltonian in a diabatic basis that spans the symmetry-induced twofold electronic degeneracy:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & P_{4} & As_{4} \textsuperscript{b} & Sb_{4} \textsuperscript{c} \\
\hline
\nu_{1} (a_{1}) & 606 & 344 & 241 \\
\nu_{2} (e) & 363 & 210 & 140 \\
\nu_{3} (t_{2}) & 464.5 & 255 & 179 \\
\hline
\end{tabular}
\caption{Ground state vibrational frequencies (cm\textsuperscript{-1}) of P_{4}, As_{4}, and Sb_{4}.}
\end{table}

\textsuperscript{a}From Ref. 31.
\textsuperscript{b}From Ref. 30(a).
\textsuperscript{c}From Ref. 30(b).
\[
\begin{bmatrix}
\langle \psi_+ | H_x (Q_0) | \psi_+ \rangle - E(Q) \\
\langle \psi_- | H_x (Q_0) | \psi_+ \rangle \\
\langle \psi_+ | H_x (Q_0) | \psi_- \rangle - E(Q) \\
\langle \psi_- | H_x (Q_0) | \psi_- \rangle
\end{bmatrix}
\begin{bmatrix}
a(Q) \\
b(Q)
\end{bmatrix} = 0,
\]

which accounts for evident patterns of transitions by mapping observed structure on the model of a radial oscillator combined with a free internal rotor moving on the lower sheet. The quantum states of this limit are approximately described by the simple expression:

\[
W(n,j) = n \hbar \omega + A^2 j^2,
\]

in which \( \omega \) is the characteristic frequency, \( n \) is the quantum number of the radial oscillator, and \( A \) is an internal rotation constant:

\[
A = \frac{\hbar^2}{2M\rho_0},
\]

where \( M \) is the reduced mass of the mode and \( \rho_0 \) is the radial minimum on the lower surface. \( j \) is the vibrational angular momentum quantum number, constrained to be half-odd integral by boundary conditions imposed by topological phase.

The simple picture of a system of transitions from the ground state of the neutral to vibrational levels of the cylindrically distorted adiabatic lower surface accounts well for the long progressions of the bands that characterize the first broad peaks of the spectra of \( P_x^+ \), \( As_x^+ \), and \( Sb_x^+ \). Similarly extending an adiabatic separation to the upper surface, we can calculate a harmonic set of widely spaced eigenstates of the steeper upper potential. In reality, these are, of course, imbedded in the dense manifold of states of the lower sheet, to which they are coupled by nonadiabatic terms. However, as discussed below, in exact nonadiabatic calculations based on the lower-order Hamiltonian, they survive as quasiresonances, which have been recognized in theory as useful semiclassical markers of coupling strength. Thus, we can associate the second broad maximum in the photoelectron spectra with a concentration of Franck-Condon intensity about the origin of the upper sheet, and predict additional maxima at intervals of higher energy.

Though the properties of such cone resonances, and the coupling conditions under which they can be expected to appear, are well characterized theoretically, no experimental examples exist that show oscillatory behavior beyond the broad bifurcation also evident in the photoelectron spectra. This may be a question of resolution; conventional photoelectron spectroscopy resolves well electronic separations, but tends to smear structure on the scale of vibrational progressions, particularly for heavier, lower-frequency systems. The spectra presented in Figs. 1–3 offer a higher resolution view of what are evidently strongly coupled systems. It is thus worthwhile to compare these spectra with theory at the highest feasible level of exact calculation in an effort to refine our semiclassical understanding of higher-lying quantum states in realistic strongly coupled systems.

B. Exact nonadiabatic calculations

Retaining the form of the Hamiltonian (1), which assumes a well-isolated degenerate electronic term, and

FIG. 5. Diagram showing the adiabatic potential energy surfaces of the linear \( E \equiv Jahn-Teller \) Hamiltonian. \( E(\rho,\phi) \) is plotted according to Eq. (2), for \( k = 5.75 \), a value deduced from spectral simulations to be that most appropriate for \( P_x^+ \). The floor of the potential lies at an energy of 16.5, in units of the zeroth-order harmonic frequency, below the conical intersection.

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further assuming the adequacy of a harmonic basis to describe motion in \( \mathcal{Q} \), we can write the Schrödinger equation to second order in vibrational amplitude \( \rho \) and phase \( \phi \):

\[
\begin{bmatrix}
T_N \mathbf{I} + \\
\begin{bmatrix}
\frac{\rho^2}{2} & k \rho e^{i \phi} + g \rho^2 e^{2i \phi} \\
-k \rho e^{-i \phi} + g \rho^2 e^{-2i \phi} & \frac{\rho^2}{2}
\end{bmatrix}
\end{bmatrix}
\times
\begin{bmatrix}
\chi_+ \\
\chi_-
\end{bmatrix}
= W
\begin{bmatrix}
\chi_+ \\
\chi_-
\end{bmatrix},
\]

in which nuclear kinetic energy \( T_N \) is diagonal, and coefficients \( k \) and \( g \) characterize linear and quadratic distortion terms, in units of the harmonic restoring force. We expand \( \chi_+ \) and \( \chi_- \) in a basis of isotropic harmonic oscillator wave functions:

\[
\begin{align*}
\chi_+ &= \sum a_{v,l} |v,l\rangle, \\
\chi_- &= \sum b_{v,l} |v,l\rangle,
\end{align*}
\]

where the oscillator frequency is chosen so that \( |v,l\rangle \) are eigenfunctions of the diagonal vibrational Hamiltonian. The explicit form of the expanded matrix is simplified by recognizing that the polar normal coordinates \( \rho e^{-i \phi} \) and \( \rho e^{i \phi} \) function as raising and lowering operators with respect to the \( l \) vibrational angular momentum quantum number, viz:

\[
\langle v,l | \rho e^{-i \phi} | v + 1,l + 1 \rangle = \sqrt{\frac{(v + l + 1)}{2}},
\]

\[
\langle v-1,l | \rho e^{i \phi} | v,l \rangle = \sqrt{\frac{(v - l - 1)}{2}}
\]

and, with

\[
\langle v,l | \rho^2 e^{-i \phi} | v',l' \rangle = \sum_{v',l'} \langle v,l | \rho e^{-i \phi} | v'',l'' \rangle \langle v'',l'' | \rho e^{-i \phi} | v',l' \rangle
\]

we construct nonzero matrix elements of the quadratic terms:

\[
\begin{align*}
\langle v,l | \rho^2 e^{-2i \phi} | v,l + 2 \rangle &= \sqrt{(v + l + 1)(v - l - 1)}, \\
\langle v,l | \rho^2 e^{-i \phi} | v + 2,l + 2 \rangle &= \sqrt{(v + l + 1)(v + l + 3)}, \\
\langle v,l | \rho^2 e^{-2i \phi} | v - 2,l + 2 \rangle &= \sqrt{(v - l - 1)(v - l - 3)}.
\end{align*}
\]

The resulting sparse matrix is diagonalized to obtain level energies and spectral overlaps.

### C. Distortion and hindered fluxionality in the ground state of \( P_2^+ \)

The vibronic spectrum of the conical intersection is particularly simple for the case in which it is assumed that \( g = 0 \).

The problem then block factors according to the quantum number \( j \), corresponding to the half-odd integral vibrational angular momentum, and only blocks with \( j = \pm 1/2 \) carry transition intensity. Under such conditions, fully converged calculations can be extended over a large range of energy using conventionally available diagonalization subroutines. Figure 6 shows a correlation diagram giving the relative energies of the first few excited states of the linearly coupled Hamiltonian as a function of the stabilization energy, \( D = 1/k^2 \), from \( D = 0 \) to the adiabatically separable limit. Figure 7 compares theoretical positions and intensities with experimental results for \( P_2^+ \), for a model that assumes single-mode linear coupling with \( k = 5.75 \) in units of the zeroth-order frequency, which is taken to be 315 cm\(^{-1}\), the experimentally observed vibrational spacing. It can be seen that the theory and experiment agree very well, particularly in the qualitative shape of the first broad maximum and the leading edge of the second band. The fit of the theoretical envelope to the experimental one yields an improved estimate of the adiabatic ionization threshold, 8.95 eV, which is difficult to obtain from the experimental photoelectron spectrum. With reference to Fig. 5, the John–Teller stabilization energy of \( P_2^+ \) in this simple linear model is 0.65 eV, which places the conical intersection at an ionization potential of 9.60 eV, and fully 15 levels of radial oscillation between the zero point and the beginning of the upper sheet. Theoretical intensities show a slight modulation in the upper range of the spectral envelope associated with the cone-resonances phenomenon noted above. Experimental limitations imposed by resolution together with the proximity of the (2t\(_1\))\(^{-1}\) transition prevent the confirmation of such structure in the data, though the band shape observed certainly does not rule out this intensity pattern.

The question of the subtle pattern of intensities and the
degree to which they match the predictions of the simple linear model is one of qualitative importance. If a system such as P₄⁺ is accurately described by a Hamiltonian coupled strictly to first order in the distortion coordinates, it then follows that the potential in these coordinates is cylindrically symmetric, presenting no barrier to vibronic pseudorotation. Under such circumstances, we must characterize the system not only as strongly distorted, but highly excipional as well. If, on the other hand, theory requires higher-order coupling terms to account for spectral positions and intensities, we must then recognize potential barriers that quench free rotation in the phase of the distortion for the lowest radial levels.

Diagonalizing the electronic part of the problem as in Eq. (1) for the explicit matrix elements expressed in the linear-plus-quadratic Hamiltonian (5) yields a more complex adiabatic potential:

$$E_\pm (\rho, \phi) = \frac{1}{2} \rho^2 \pm k \rho \left[ 1 + \frac{8 \rho}{k} \cos(3\phi) + \frac{8 \rho^2}{4k^2} \right]^{1/2}. \quad (16)$$

For small $g/k$, this expression simplifies to read

$$E_\pm (\rho, \phi) = \left[ \rho^2 \pm 2g\rho \cos(3\phi) \right] \pm k\rho \quad (17)$$

using Eq. (17) to identify maxima and minima in the floor of the lower sheet, we can solve for the pseudorotation barrier as a function of $k$ and $g$:

$$E(\rho_0, \phi_{\text{max/min}}) = \frac{k^2}{2(1 \pm g)}. \quad (18)$$

The matrix elements that produce these modulations couple vibrational basis states in a scheme that block factors as $j' = j \mod 3$. As a result, with reference to the correlation diagram in Fig. 6, the accidental degeneracy eigenstates of the linear-only Hamiltonian with $j = \pm 3/2, 9/2, 15/2, \ldots$ split, and other levels, which are closely lying in the linear approximation and belong to the same $j'$ block, similarly diverge and share intensity. Figure 8 illustrates the effect of including quadratic coupling in the simulated spectrum of P₄⁺, retaining the linear parameter of Fig. 7. As can be seen, by distributing the oscillator strength of the radical fundamentals over all the added states of the $j = \pm 1/2\mod 3$ block, higher-order coupling greatly increases the density of allowed transitions. Interestingly, however, broader intensity patterns are less affected, and when simulated spectra are convoluted with a 15 meV instrumental function, the overall band shape remains roughly constant over the full range of quadratic coupling for which we can obtain converged intensities.

However, one important trend can be recognized. For $g = 0$, the family of transitions to the $j = 1/2\mod 3$ fundamentals form a highly regular progression of bands. The addition of quadratic barriers of a magnitude comparable to the zero-point energy initially disrupts this structure, spreading intensity over an irregular distribution of states, and thus smoothing the leading edge of the first band for values of $g$ that fall in the range from 0.005 to 0.02. For $g$ greater than 0.02 quadratic pseudorotation barriers significantly exceed the radial vibrational frequency. These larger modulations of the pseudorotation most trap lower-lying vibrational states in threefold wells. The associated vibrational structure tends toward that of statically distorted isomers, with an increased periodicity, broken by tunneling splitting and above-barrier reflection. As a result, we recognize that lower and higher extremes of quadracc coupling are spectroscopically characterized by periodic intensity modulations. The P₄⁺ spectrum displays sufficient resolution to show periodic structure on the trailing edge of the first band. But, the leading edge of this band is comparatively smooth. Such behavior is encompassed by only a relatively narrow range of quadratic coupling coefficients, including $g$ from about 0.01 to 0.02.

Thus, we have a quantitative picture of the Jahn–Teller coupling in the $^2E$ state of P₄⁺ that is reasonably secure to second order. The largest term coupling the electronic degeneracy is linear in the $\nu$ vibrational coordinate, producing a strong distortion, stabilized by 0.65 eV relative to the symmetric configuration. The resulting vibronic pseudorotation trough is modulated by a moderate higher-order coupling, which erects a threefold barrier with a height comparable to the zero-point energy. A potential energy surface illustrating the relative magnitude of these effects is presented in Fig. 9. The principal observable consequence of the dominant linear distortion is the transfer of Franck-Condon intensity to transitions that produce vibronically excited ions, which form a spectrum with a distinctive double maximum. By quenching vibronic angular momentum, quadratic coupling widens this intensity distribution to include transitions forbidden under conditions of linear coupling alone, which, at the level appropriate to explain the P₄⁺ spectrum, smooths the leading edge of the first band.
D. Strong vibronic couplings in As$_2^+$ and Sb$_2^+$: The cases for cone resonances in realistic systems

The qualitative features of the $(1e)^{-1}$ bands of As$_2^+$ and Sb$_2^+$ are similar to that of P$_2^+$ and can be interpreted similarly. However, it is more difficult to be as precise in our vibronic assessments of As$_2^+$ and Sb$_2^+$. Neither spectrum exhibits discernable structure that can be associated with individual vibrational bands. Nevertheless, the neutral ground state frequencies are known,$^{32}$ and a simple linear approach can be used just as with P$_2^+$ to characterize the gross properties of vibronic distortions responsible for the observed photoelectron spectra. Figures 10 and 11 show our spectral simulations for linear coupling parameters of

FIG. 8. Spectral simulations of P$_2^+$ spectrum constructed by convoluting theoretical positions and intensities (sticks), calculated for $k = 5.75$ and $g$ from 0 to 0.1, with a 15 meV FWHM Gaussian instrumental function. Theoretical positions and intensities for $g > 0$ were obtained by diagonalizing Eq. (5) iteratively in a basis of 1302 isotropic two-dimensional harmonic oscillator wave functions using the Lanczos method (Ref. 32). (a) $g = 0$; (b) $g = 0.005$; (c) $g = 0.008$; (d) $g = 0.01$; (e) $g = 0.02$; (f) $g = 0.05$; (g) $g = 0.1$.

FIG. 9. Diagram illustrating the adiabatic potential energy surfaces of the linear plus quadratic $E$ in $e$ Jahn–Teller Hamiltonian. $E(\rho, \phi)$ is plotted according to Eq. (17), for $k = 5.75$ and $g = 0.02$. The floor of the potential is modulated by three barriers that extend to a height of 0.66 in units of the zeroth-order harmonic frequency.

FIG. 10. Linear Jahn–Teller fit to the $(1e)^{-1}$ band of the As$_2^+$ photoelectron spectrum. The linear coupling parameter $k$ in units for which the harmonic force constant is 1, is 9.7. The progression of transitions to $j = 1/2$ radial harmonics originates at an adiabatic ionization energy of 7.83 eV. Positions and intensities were obtained as in Fig. 7.
TABLE III. Estimated adiabatic ionization potentials (IPs) and Jahn–Teller stabilization energies (D) for the (1e) band of P⁺⁺, As⁺⁺, and Sb⁺⁺.

<table>
<thead>
<tr>
<th></th>
<th>P⁺⁺</th>
<th>As⁺⁺</th>
<th>Sb⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP (eV)</td>
<td>8.95</td>
<td>7.83</td>
<td>6.61</td>
</tr>
<tr>
<td>D (eV)</td>
<td>0.65</td>
<td>0.84</td>
<td>1.4</td>
</tr>
</tbody>
</table>

FIG. 11. Linear Jahn–Teller fit to the (1e)⁻¹ band of the Sb⁺⁺ photoelectron spectrum. The linear coupling parameter k in units for which the harmonic force constant is 1, is 12.5. The progression of transitions to j = 1/2 radial harmonics originates at an adiabatic ionization energy of 6.61 eV. Positions and intensities were obtained as in Fig. 7.

The calculated frequencies are so much smaller, the potential surfaces of the heavier systems contain many more adiabatically separable vibronic states; respective pseudopotential troughs support about 45 overtones of the radial oscillation for As⁺⁺, and nearly 80 for Sb⁺⁺.

The derived adiabatic ionization potentials and the Jahn–Teller stabilization energies for the three cluster ions are summarized in Table III.

V. CONCLUSIONS

First photoelectron bands P⁺⁺, As⁺⁺, and Sb⁺⁺ have been analyzed in detail in terms of the vibronic consequences of E = e Jahn–Teller coupling. For P⁺⁺, spectral simulations for linear coupling with a constant of k = 5.75 agree well with experiment. Refinement in terms of higher-order coupling terms improves the agreement between theory and experiment. Best fits add small quadratic terms to the same linear distortion, predicting quadratic barriers to pseudorotation comparable to the zero-point energy. Thus, P⁺⁺ is characterized in its ground vibronic state as both highly distorted and highly fluxional. Cone resonances appear in the calculated spectra, but appear disrupted by higher-order coupling in real systems. Linear-only calculations on As⁺⁺ and Sb⁺⁺ also agree well with the experiment, though the effects of higher-order couplings remain evident. Quantitative account of vibronic coupling is essential for accurate estimate of adiabatic ionization potentials.

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