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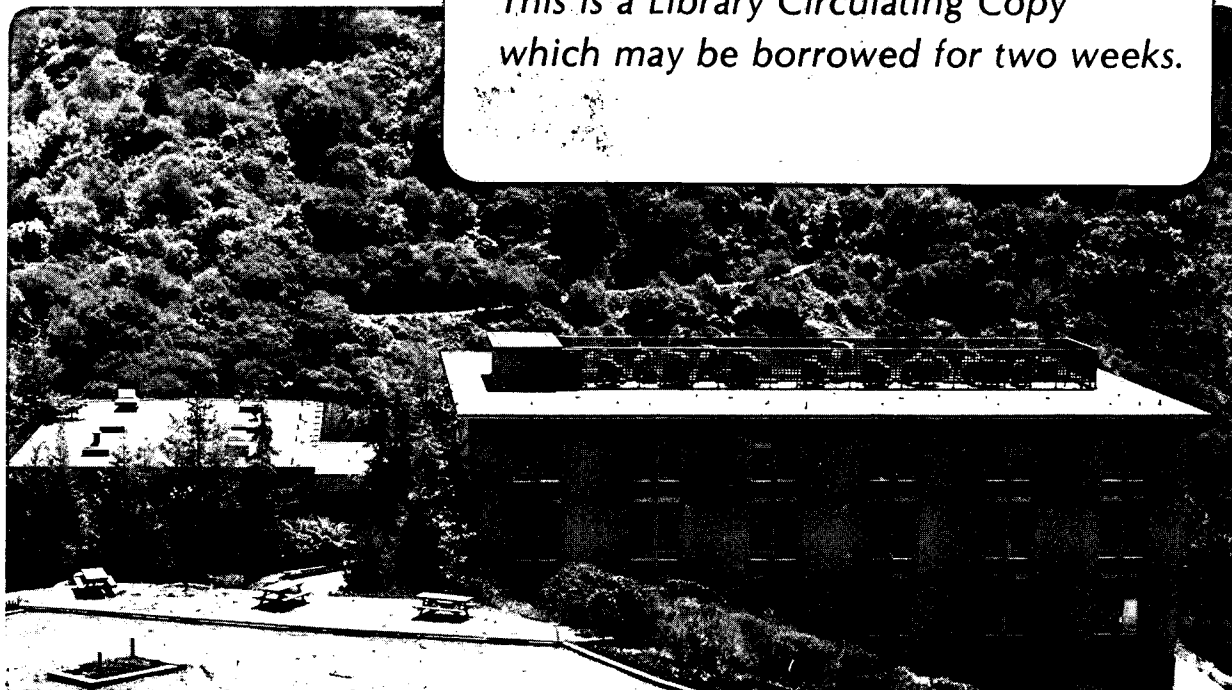
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March 1989

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# Vibrational Spectra of $Se_2^+$ and $Te_2^+$ in Their Ground States

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# Abstract

Vibrationally-resolved photoelectron spectra of $Se_2^+$ and $Te_2^+$ in their ground states were measured using a newly-constructed high temperature supersonic molecular beam source. Ionization potentials and fundamental spectroscopic constants for the molecular ions were obtained.

## 1. Introduction

Photoelectron spectroscopy (PES) not only yields electronic binding energies, but a well-resolved molecular PE spectrum can also be analyzed to derive the spectroscopic constants of the molecular ion. Especially for diatomic molecules, such parameters as the vibrational frequency and the equilibrium bond length can be obtained. It is therefore important to resolve the vibrational fine structure in PES.

The HeI (584Å) PE spectra of the Group VI diatomics have all been reported: $O_2$ [1,2], $S_2$ [3,4], $Se_2$ [5,6],$Te_2$ [4-6], but vibrationally-resolved spectra were obtained for only $O_2$ [1,2] and $S_2$ [3]. To resolve vibrational structure in $Se_2$ and $Te_2$ requires much higher resolution, because the vibrational frequencies are much smaller, and it also may be necessary to use supersonic molecular beams to cool the molecules internally.

The vibrationally-resolved PE spectra of $Se_2$ and $Te_2$ are especially interesting, because the relativistic effects are expected to play an increasingly important role going down the Periodic Table [7]. As a matter of fact, relativistic effects have already been invoked to interpret the anomalous $^2\Pi_{g1/2}$ / $^2\Pi_{g3/2}$ intensity ratio in the PE spectra of $S_2$, $Se_2$,and $Te_2$ [8]. Therefore, spectroscopic information derived from vibrationally-resolved PE spectra can be used directly to compare with relativistic quantum chemistry calculations.

In this letter, we report vibrationally-resolved PE spectra of $Se_2^+$ and $Te_2^+$ in their ground states, using our recently built high-temperature supersonic molecular beam source. A Franck-Condon analysis was used to obtain the equilibrium bond lengths of the respective molecular ions.

## 2. Experimental

The vapors of elemental Se and Te are equilibrium mixtures of 2-6 atom clusters [9]. The best ways to produce the diatomics are either to use a double oven set-up or to start with alloys of the elements [5]. $Te_2$ can also be generated from the pure element by carefully controlling the temperature [4]. The spectra reported in this letter were obtained during our study of SnSe and SnTe. $Se_2$ and $Te_2$ were formed as "outgas" molecules during the preheating periods of the respective samples at about 720K for $Se_2$ and 1070K for $Te_2$. The outgas processes were slow enough for us to take the spectra shown in this letter.

The details of the high temperature molecular beam source will be published separately. A diagram of the oven system is shown in Fig. 1. Basically, it uses electron bombardment heating to avoid the stray fields associated with the simpler resistive heating method. The main components consist of a 0.51 mm Tungsten filament, a Molybdenum electrostatic deflector, a Tungsten vacuum jacket and a graphite crucible. Various types of sample boats can be used with the graphite crucible. However, the samples were loaded directly into the crucible in the current experiments. The nozzle sizes used were 0.152 mm for $Se_2$ and 0.127 mm for $Te_2$. A He carrier gas pressure of 150 torr was used for $Se_2$ and 200 torr Ne was used for $Te_2$. The SnSe and SnTe compounds were commercial samples from CERAC.

The molecular beam PE spectrometer was described in detail elsewhere [10]. Briefly, it consists of the molecular beam source, a rare gas discharge lamp, a quadrupole mass spectrometer, and an electrostatic hemispherical electron analyzer with a multichannel detector. Ar PE peaks were usually used as the kinetic energy calibration. Normally, the energy resolution was about 13 meV at 1 eV pass energy. It was degraded slightly under the current high temperature condition.


3. Results and discussion


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The PE spectra of $Se_2^+$ and $Te_2^+$ in their ground states are shown in Fig. 2 and Fig. 3, where the dotted spectra are experimental and the line spectra are theoretical, calculated from the Franck-Condon factors (see below). The $Se_2^+$ spectrum consists of two partially-overlapping bands, as a result of the spin-orbit splitting. The Franck-Condon factors of only the $^2\Pi_{g1/2}$ state are plotted. In the $Te_2^+$ spectrum, the $^2\Pi_{g3/2}$ band, with an ionization energy of about 0.47 eV higher [4,6], was not observed, both because it overlapped with the $SnTe^+$ spectrum and because its intensity was some ten times smaller than that of the $^2\Pi_{g1/2}$ band [4,6,8]. The ionization potentials (IPs) for both molecules are listed in Table 1. As can be seen from the Table, the first peak in each spectrum is a hot band transition. Vibrational temperatures of 350K and 300K fit very well for $Se_2$ and $Te_2$, respectively. This demonstrates the advantage of using supersonic molecular beams. We could not make a good estimate of the rotational temperatures, which are expected to be much lower than the respective vibrational temperatures. Part of the linewidths in our spectra, which are higher than the instrumental resolution, is due to the rotational broadening.

The Franck-Condon factor analysis is similar to that used in Ref. [11]. Basically, we applied a Morse oscillator, described by expansion as a power series of $(r - r_e)$. The $(r - r_e)^3$ and $(r - r_e)^4$ terms were taken as perturbation corrections to the harmonic oscillator Hamiltonian. In Figs. 2 and 3 are plotted the best Franck-Condon fits, which yielded the equilibrium bond lengths of the respective ionic states as listed in Table 2. The vibrational frequencies and the bond dissociation energies are also tabulated in Table 2. In the case of $Se_2^+$, an accurate value of $2126 \pm 10$ $cm^{-1}$ for the spin-orbit splitting was also derived.

Based on the spectroscopic constants given in Table 2, the related Morse potentials can be calculated. They are shown in Figs. 4 and 5. Since ionization removes an electron from the anti-bonding $\Pi_g$ orbital in both $Se_2^+$ and $Te_2^+$, the chemical bonds become stronger in the ionic states. This leads to shortening of the equilibrium bond lengths, and increases of both the vibrational frequencies and the bond dissociation energies in the ionic

states. In $Se_2^+$, we can conclude that the $^2\Pi_{g1/2}$ state is slightly more strongly bound than the $^2\Pi_{g3/2}$ state. It is also interesting to note that, fractionally, the bonds in $Se_2^+$ and $Te_2^+$ seem to be more strengthened than that in $S_2^+$[3].

In conclusion, we have obtained the high resolution PE spectra of $Se_2^+$ and $Te_2^+$ in their ground states. Fundamental spectroscopic constants were derived for the molecular ions, and the advantages of using supersonic molecular beams in high temperature PES were demonstrated.

Acknowledgement

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Table 1

The ionization potentials of $Se_2$ and $Te_2$.

| | | IP (eV)[a] | v | Intervals |
|---|---|---|---|---|
| $Se_2^+$ | $^2\Pi_{g1/2}$ | 8.7230 | hot band | |
| | | 8.7711 | 0 | 0.0481 |
| | | 8.8281 | 1 | 0.0570 |
| | | 8.8845 | 2 | 0.0564 |
| | | 8.9409 | 3 | 0.0564 |
| | | 8.9915 | 4 | 0.0506 |
| | $^2\Pi_{g3/2}$ | 9.0387 | 0 | |
| | | 9.0942 | 1 | 0.0555 |
| | | 9.1494 | 2 | 0.0552 |
| | | 9.2043 | 3 | 0.0549 |
| $Te_2^+$ | $^2\Pi_{g1/2}$ | 8.1574 | hot band | |
| | | 8.1872 | 0 | 0.0298 |
| | | 8.2234 | 1 | 0.0362 |
| | | 8.2581 | 2 | 0.0347 |
| | | 8.2928 | 3 | 0.0347 |

a. The uncertainty for the absolute IPs is ± 0.006 eV. The extended accuracy quoted in the table only has significance when one takes the intervals whose uncertainties are ± 0.0010 eV.

Table 2

The derived spectroscopic constants for $Se_2^+$ and $Te_2^+$, together with the respective neutral ground states [12].

| | | $\omega_e$ (cm$^{-1}$) | $r_e$ (Å) | $D_0$ (eV)[a] | A (cm$^{-1}$) |
|---|---|---|---|---|---|
| $Se_2$ | $^3\Sigma_g^-$ ($0_g^+$) | 385.303 | 2.1660 | 3.411 | |
| $Se_2^+$ | $^2\Pi_{g1/2}$ | 450 ± 10 | 2.072 ± .005 | 4.37 | |
| | $^2\Pi_{g3/2}$ | 443 ± 10 | 2.080 ± .005 | 4.38 | 2126 ± 10 |
| $Te_2$ | $^3\Sigma_g^-$ ($0_g^+$) | 247.070 | 2.5574 | 2.677 | |
| $Te_2^+$ | $^2\Pi_{g1/2}$ | 282 ± 10 | 2.489 ± .005 | 3.50 | |

a. The accuracy of the $D_0$ values for the ionic states is limited by the accuracy of the atomic IPs, see Ref. [13].
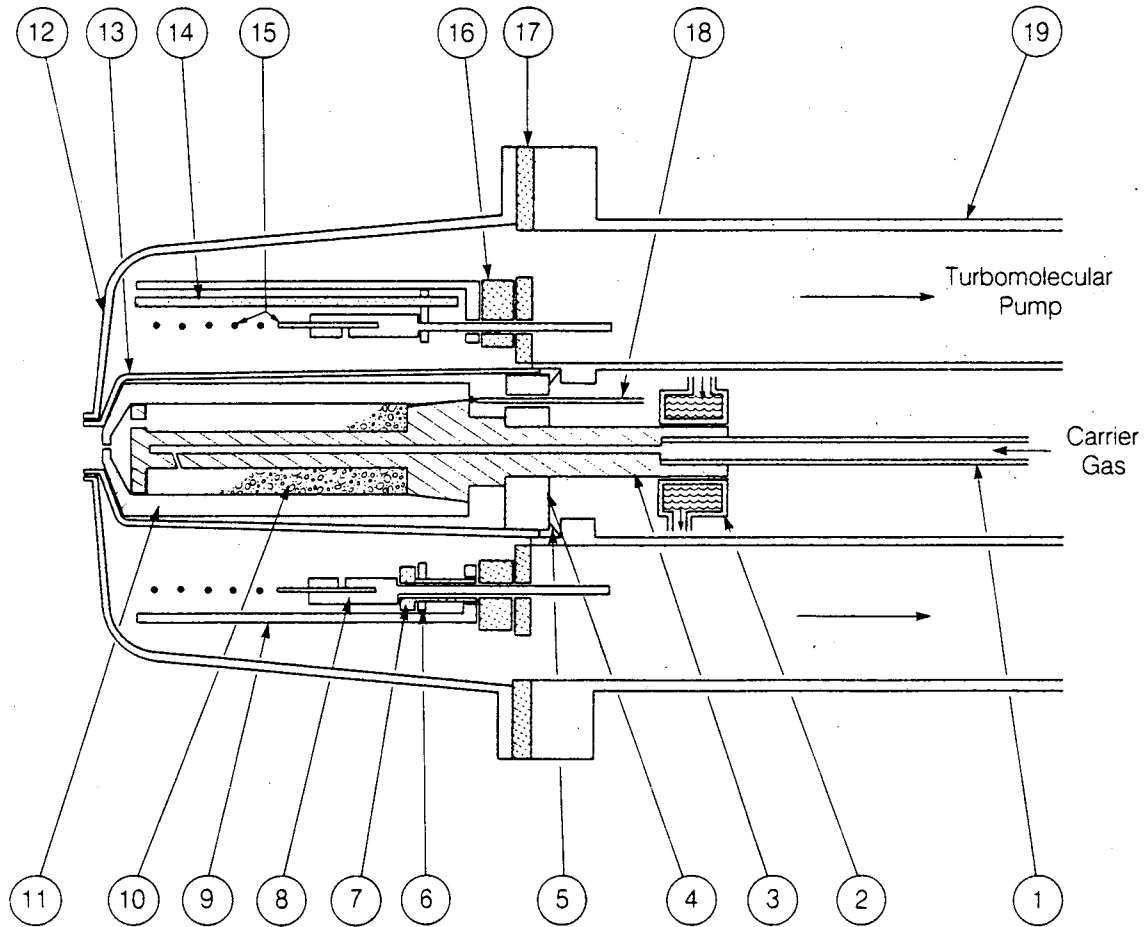
Figure captions

Figure 1. A cross sectional view of the oven assembly. (1) Ta carrier gas inlet tube, (2)
water cooling block, (3) graphite crucible cap, (4) graphite radiation shield,
(5) Mo springy conduction barrier, (6) Mo retainer, (7) ceramic insulator, (8)
Mo filament mount post, (9) Mo electrostatic deflector and radiation shield, (10)
sample, (11) graphite crucible body, (12) outer W vacuum jacket, (13) inner W
vacuum jacket, (14) ceramic filament support rod, (15) W filament, (16)
ceramic high voltage standoff, (17) ceramic support plate for filament post, (18)
thermocouple, (19) stainless steel triple-tubed flange section (shown in two-fold
symmetry for easier viewing). Not shown are the bus lines, some radiation
shields, and W wires for supporting the filament.

Figure 2. The PE spectrum of $Se_2^+$, $^2\Pi_{g1/2}$ and $^2\Pi_{g3/2}$ states. HB is a hot band
transition. ( ... experimental spectrum, — calculated FCFs).

Figure 3. The PE spectrum of $Te_2^+$, $^2\Pi_{g1/2}$ state. HB is a hot band transition.
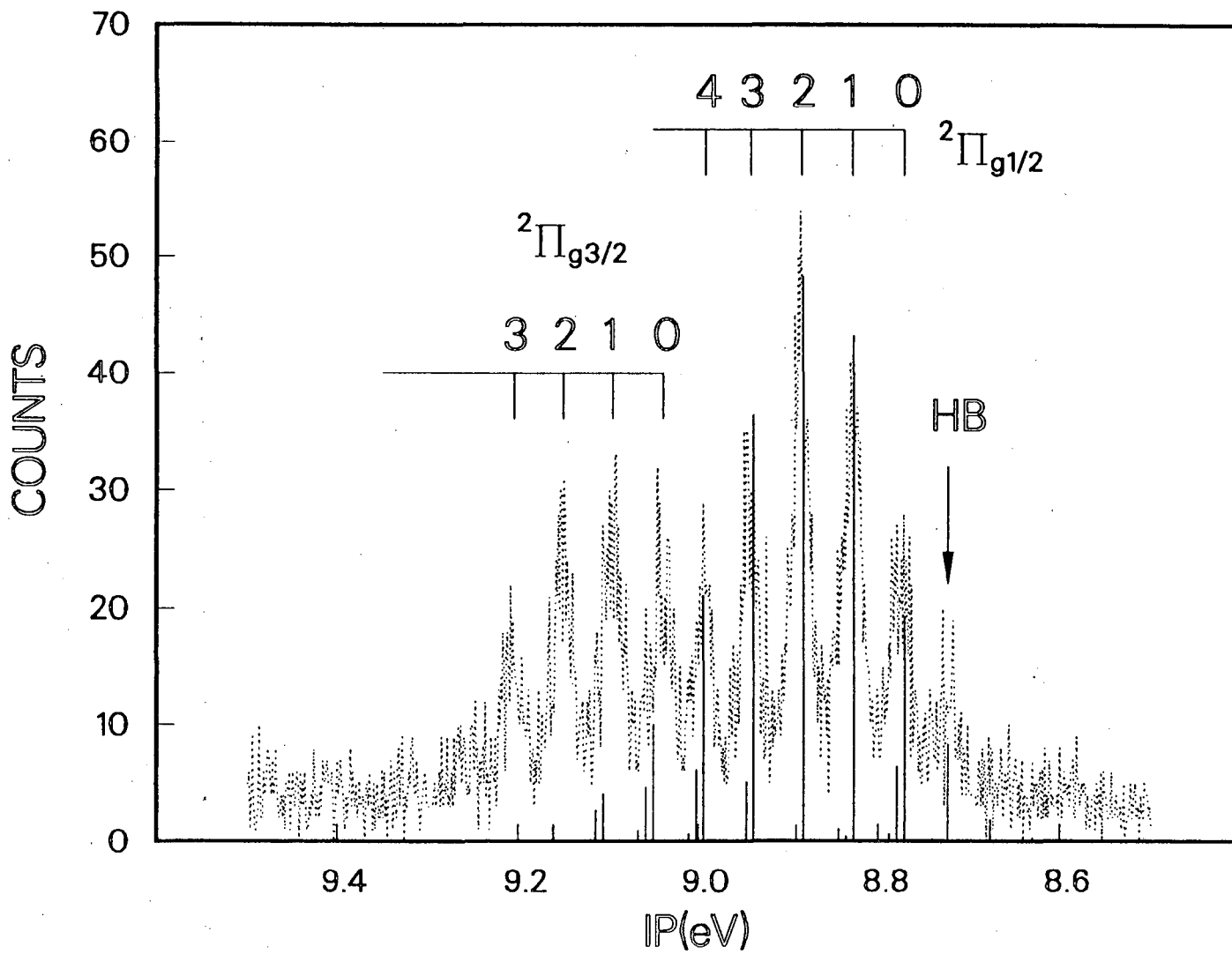( ... experimental spectrum, — calculated FCFs).

Figure 4. The Morse potentials for the transitions $Se_2^+$ $^2\Pi_{g1/2,3/2}$ ← $Se_2$ $^2\Sigma_g^-$ $(O_g^+)$.

Figure 5. The Morse potentials for the transition $Te_2^+$ $^2\Pi_{g1/2}$ ← $Te_2$ $^2\Sigma_g^-$ $(O_g^+)$.

Turbomolecular Pump

Carrier Gas

XBL 8712-10503

Figure 1

Figure 2

XBL 893-1004

13

Figure 3

XBL 893-1005

14

$Se^+(^4S)+Se(^3P)$

$^2\Pi_{g3/2}$

$^2\Pi_{g1/2}$

$Se(^3P)+Se(^3P)$

$^3\Sigma_g^-(0_g^+)$

POTENTIAL ENERGY (eV)

BOND LENGTH (Å)
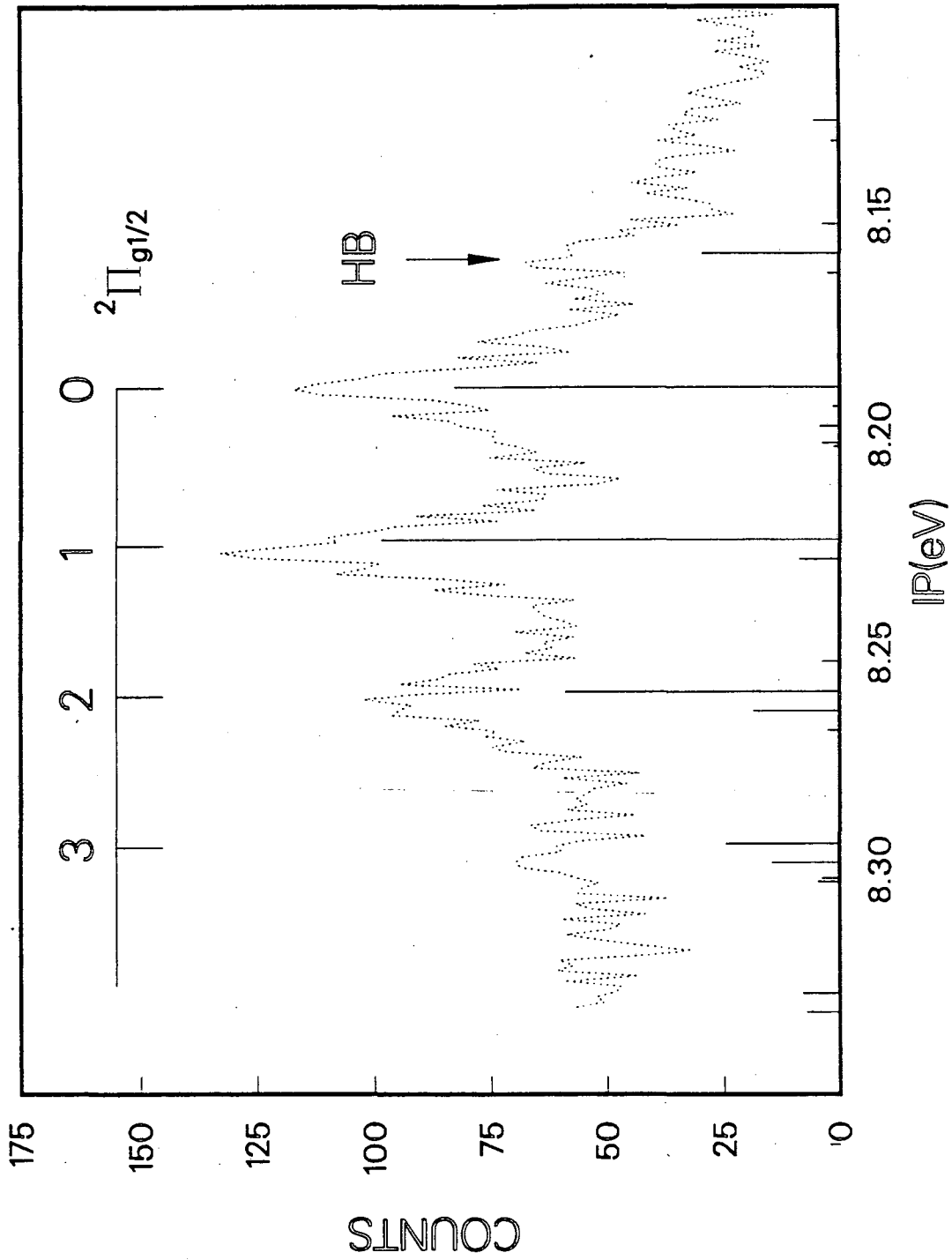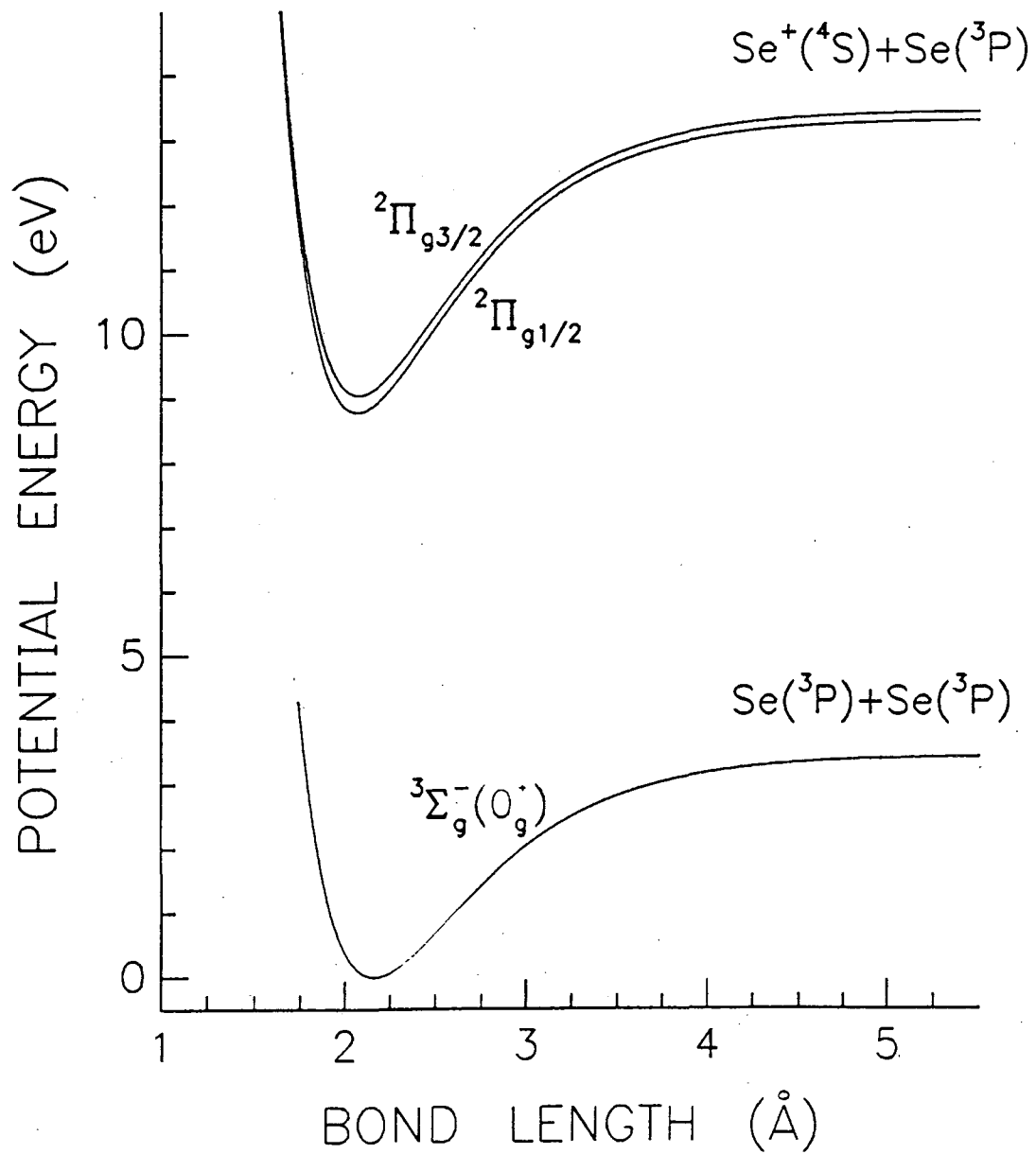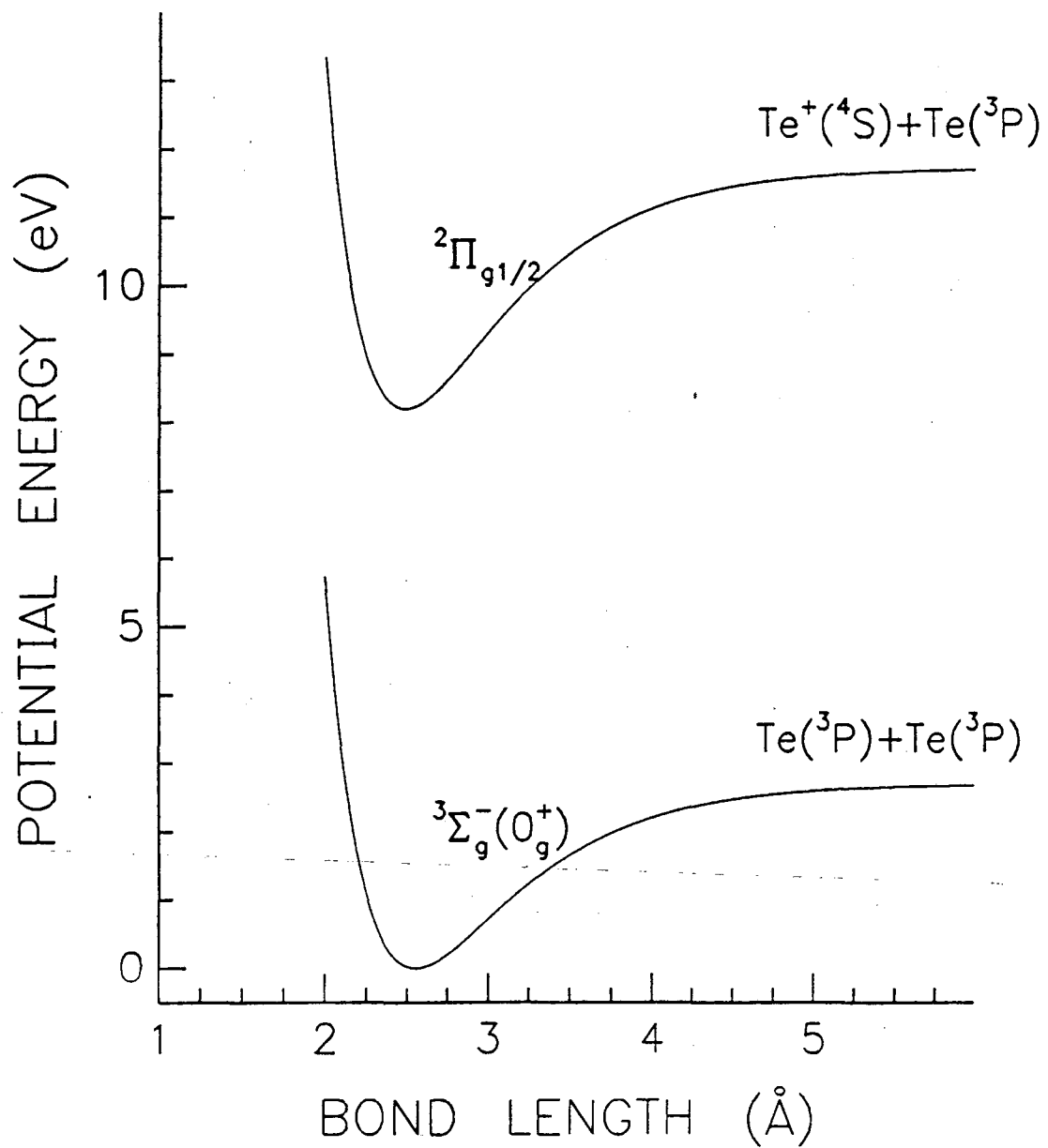
XBL 893-1002

Figure 4

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Figure 5

XBL 893-1003

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