

VIBRATIONAL SPECTRA OF Se_2^+ AND Te_2^+ IN THEIR GROUND STATES

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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 (584 Å) 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 “out-gas” molecules during the preheating periods of the respective samples at about 720 K for Se_2 and 1070 K for Te_2 . The outgas processes were slow enough for us to take the spectra 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

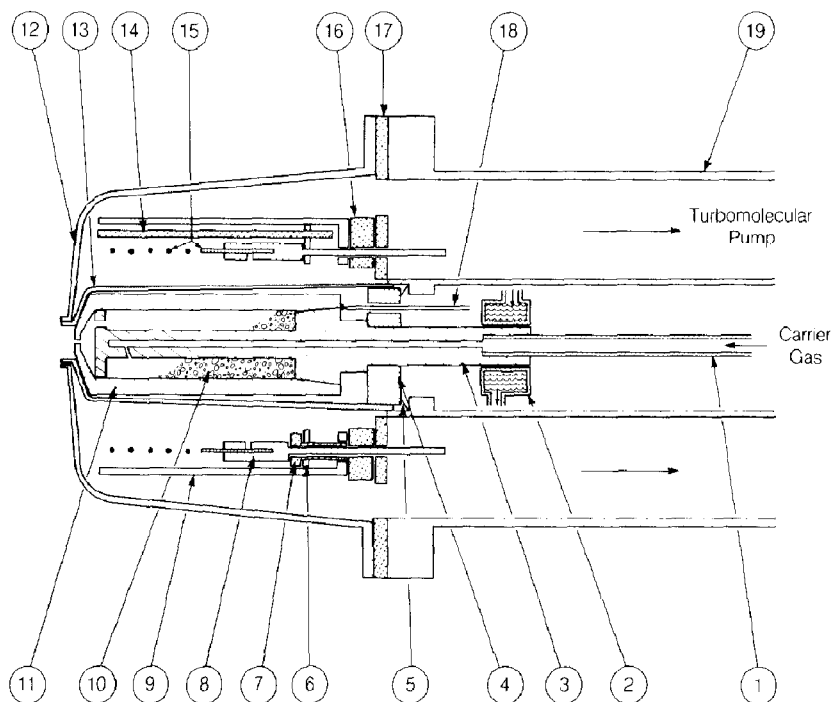


Fig. 1. A cross-sectional view of the oven assembly. (1) Ta carrier gas inlet tube, (2) water cooling block, (3) graphite crucible cap, (4) graphite radiation shield, (5) Mo springy conduction barrier, (6) Mo retainer, (7) ceramic insulator, (8) Mo filament mount post, (9) Mo electrostatic deflector 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 twofold symmetry for easier viewing). Not shown are the bus lines, some radiation shields, and W wires for supporting the filament.

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

The PE spectra of Se_2^+ and Te_2^+ in their ground states are shown in figs. 2 and 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 350 and 300 K fit very well for Se_2 and Te_2 , respec-

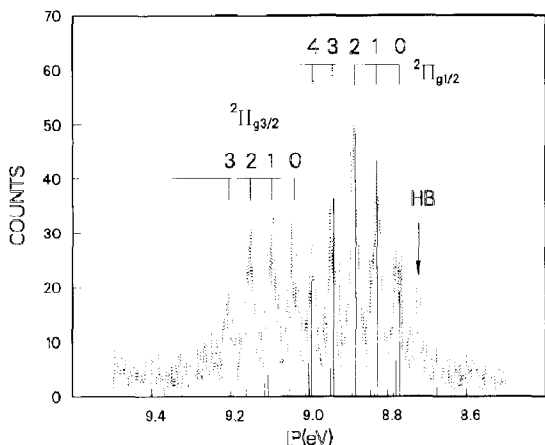


Fig. 2. The PE spectrum of Se_2^+ , ${}^2\Pi_{g1/2}$ and ${}^2\Pi_{g3/2}$ states. HB is a hot band transition (... experimental, — calculated FCFs).

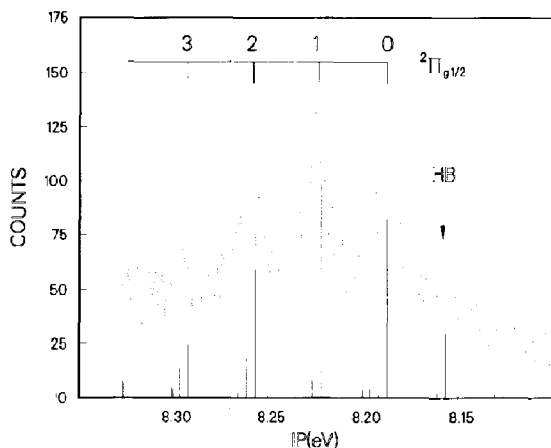


Fig. 3. The PE spectrum of Te_2^+ , ${}^2\Pi_{g1/2}$ state. HB is a hot band transition (... experimental spectrum, — calculated FCFs).

tively. This demonstrates the advantage of using supersonic molecular beams. We could not make a good estimate of the rotational temperatures, which

Table 1
The ionization potentials of Se_2 and Te_2

	IP ^{a)} (eV)	ν	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.

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 $2126 \pm 10 \text{ cm}^{-1}$ for the spin-orbit splitting was also derived.

Table 2
The derived spectroscopic constants for Se_2^+ and Te_2^+ , together with the respective neutral ground states [12]

	ω_e (cm^{-1})	r_e (Å)	D_0 ^{a)} (eV)	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 ± 0.005	4.37	
	${}^2\Pi_{g3/2}$	443 ± 10	2.080 ± 0.005	4.38
Te_2 ${}^3\Sigma_g^-(0_g^+)$	247.070	2.5574	2.677	
Te_2^+ ${}^2\Pi_{g1/2}$	282 ± 10	2.489 ± 0.005	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].

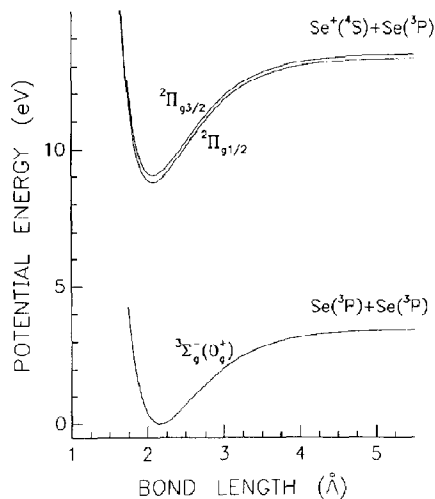


Fig. 4. The Morse potentials for the transition $\text{Se}_2^+ \ ^2\Pi_{g1/2,3/2} \leftarrow \text{Se}_2 \ ^2\Sigma_g^-(0_g^+)$.

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 antibonding Π_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.

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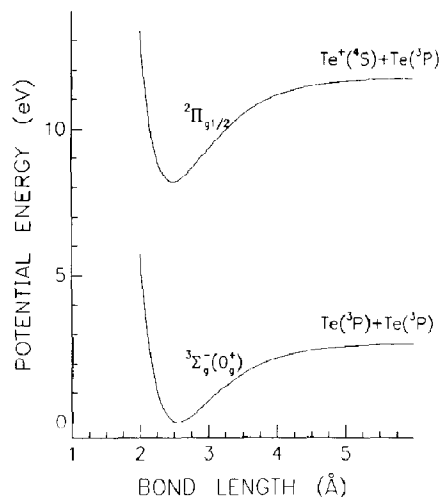


Fig. 5. The Morse potentials for the transition $\text{Te}_2^+ \ ^2\Pi_{g1/2} \leftarrow \text{Te}_2 \ ^2\Sigma_g^-(0_g^+)$.

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