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Relativistic Effects in the UV Photoelectron Spectra of Group VI Diatomic Molecules

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ABSTRACT

The anomalous $^2\Pi_{1/2}/^2\Pi_{3/2}$ intensity ratios observed recently in the photoelectron spectra of S_2, Se_2, and Te_2 are shown to arise from spin-orbit coupling in the ground state. An intermediate coupling calculation gives good agreement with all observed intensity ratios and predicts a ratio of $\sim$35 in Po_2.

The HeI photoelectron spectra of the group VI homonuclear diatomics, O_2,[1,2] S_2,[3,4] Se_2,[5] and Te_2[4,5] have all been reported. In every case, the spin-orbit (s-o) components of the $X^2\Pi_g$ ionic state were resolved. The branching ratio of $^2\Pi_{1/2}/^2\Pi_{3/2}$ (the subscript g is dropped for simplicity) was found to be increasingly larger than 1, the statistical ratio, with increasing molecular weight (Table I), and for Te_2, the ratio reached a dramatic value of 10. Berkowitz and coworker[4,5] attempted to explain this intensity variation as follows. During the photoionization the allowed transitions $\Delta\Omega = 0$ were postulated to be strongly preferred to $\Delta\Omega = \pm 1$, as was observed in the absorption spectra of Se_2[6] and TeO[7] in the visible and near UV region. In addition, the continuum photoelectrons resulting from photoionization were postulated to have a strong preference for the $\varepsilon p\sigma$, rather than $\varepsilon p\pi$, channel. These additional constraints, together with the ground state of the heavier diatomic chalcogens being more appropriately described as $X0_g^+$, rather than $X^3\Sigma_g^-$ as a result of Hund's coupling case (c) would account for the greater intensity of the $^2\Pi_{1/2}$ peak in Te_2^+, relative to $^2\Pi_{3/2}$. The smaller $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratios in lighter diatomics than Te_2 were attributed to contributions from the $X1_g$ state, populated thermally because of smaller $X1_g$ - $X0_g^+$ splitting.

We note however, the above explanation is unsatisfactory if applied to other heavy linear molecules, where Ω is more nearly a good quantum number in the ions and neutral molecules. The same arguments[4,5] would then predict intensity ratios $^2\Pi_{1/2}/^2\Pi_{3/2}$ much larger than unity in photoionization, because 0^+ is normally the ground state. This, however, is not the case; for example, in I_2 [8] and Bi_2 [9] the ratio is close to 1.

Furthermore, to draw an analogy between photoionization and photoabsorption to a valence state involving different MO's might be invalid. In this communication, we offer an alternative explanation for the observed $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratios in dichalcogens. Our approach requires no assumptions about the dynamics of photoionization, but the effects of intermediate coupling on the $\pi_{1/2}$ - $\pi_{3/2}$ composition of the ground state are taken into account.

Recently, we reported relativistic effects in the photoelectron spectrum of Pb vapor,[10] which caused the observed branching ratio of $^2P_{1/2}/^2P_{3/2}$ in Pb^+ to be 14.1 as opposed to the statistical value of 0.5 expected in L-S coupling. This is a consequence of the ground state of Pb being best approximated in terms of j-j coupling as $(p_{1/2})^2$ with a small configuration interaction (CI) admixture of $(p_{3/2})^2$; i.e., $\Psi = a(p_{1/2})^2_0 + b(p_{3/2})^2_0$; with $a^2/b^2 \sim 14$. We believe a similar phenomenon happens with the heavier Group VI diatomics, except that here we have the molecular analogue. As the s-o coupling gets stronger, it becomes more appropriate to describe the coupling of angular momenta in diatomics in Hund's case c rather than case b (or a) coupling.[11,12] If only the electronic states are considered, this is identical to using ω-ω rather than Λ-Σ coupling,[12] the molecular equivalents of j-j and L-S couplings respectively. In ω-ω coupling, the $\vec{\ell}\cdot\vec{s}$ interaction splits the π molecular orbital (MO) into ω = 1/2 and 3/2 orbitals; with the former being lower in energy. For Group VI diatomics with the π^2 configuration, this gives rise to three configurations and four states; i.e., $(1/2,1/2)_0$, $(1/2,3/2)_{1,2}$, and $(3/2,3/2)_0$ (where the subscripts denote Ω, the axial projection of the total electronic angular momentum). The ground state of π^2 (Ω = 0) can then be approximated in ω-ω coupling by a simple CI expansion

$$\Psi(X0_g^+) = a(1/2,1/2)_0 + b(3/2,3/2)_0. \qquad (1)$$

If we neglect the difference in the $\pi_{1/2}$ and $\pi_{3/2}$ photoionization cross sections (which in any event should be small), the intensity ratio $^2\Pi_{1/2}/^2\Pi_{3/2}$ is given by a^2/b^2. The relative weights of a and b depend on the strength of the $\vec{\ell}\cdot\vec{s}$ interaction. In terms of Λ-Σ coupling, eq.(1) corresponds to a mixture of $^3\Sigma_0^-$ and $^1\Sigma_0^+$ states. In the absence of s-o coupling, the ground state is (see below)

$$\Psi°(X^3\Sigma_{g,0}^- \text{ or } X0_g^+) = \frac{1}{\sqrt{2}}(1/2,1/2)_0 + \frac{1}{\sqrt{2}}(3/2,3/2)_0, \qquad (2)$$

and the $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio is 1. By constrast, if the s-o coupling is large, then the ground state will be predominantly $(1/2,1/2)_0$ and the ratio will be much greater than 1, or $X^2\Pi_{3/2}$ may hardly be detected at all. If the splitting[13] between $X^3\Sigma_0^-$ (or 0^+) and $X^3\Sigma_1$ (or 1) is not too large for the $X1_g$ state to be populated thermally, but too small to be resolved, then the experimental ratio will be altered by contribution from $X1_g$, which would give a $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio of unity.

In the following, we present a simple calculation by which the CI wave functions (eq.(1)) of Group VI diatomics can be estimated, to obtain the $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio theoretically. Because relativistic molecular wave functions are not available, we shall instead expand the nonrelativistic CI function in terms of Λ-Σ basis functions. Thus the ground state can be expressed as

$$\Psi(X^3\Sigma_{g,0}^- \text{ or } X0_g^+) = C_1\Psi°(^3\Sigma_0^-) + C_2\Psi°(^1\Sigma_0^+), \qquad (3)$$

where

$$\Psi^\circ(^3\Sigma_0^-) = A\left|\pi_g^+(1)\pi_g^-(2)(1/\sqrt{2})[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \times [\text{paired electrons}]\right|$$

and

$$\Psi^\circ(^1\Sigma_0^+) = A\left|\pi_g^+(1)\pi_g^-(2)(1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times [\text{paired electrons}]\right|. \quad (4)$$

Approximating the s-o Hamiltonian by $H_{s-o} = \sum_i \zeta_i \vec{\ell}\cdot\vec{s}_i$,[14] where ζ_i is the atomic s-o coupling constant, we then obtain the matrix elements of $H = H_o + H_{s-o}$ as follows:

	$^3\Sigma_0^-$	$^1\Sigma_0^+$
$^3\Sigma_0^-$	$E_o(^3\Sigma_0^-)$	ζ_{np}
$^1\Sigma_0^+$	ζ_{np}	$E_o(^1\Sigma_0^+)$,

where H_o is the electrostatic Hamiltonian. The expressions for E_o's can be readily obtained from eq.(4), and of relevance here is the difference $E_o(^1\Sigma_0^+) - E_o(^3\Sigma_0^-) = 2K$, i.e., two times the exchange integral between π_g^+ and π_g^- MO's. Referenced to $E_o(^3\Sigma_0^-)$, the solutions of the corresponding secular equation are $E = K \pm \sqrt{K^2 + \zeta_{np}^2}$ and $C_2/C_1 = E/\zeta_{np}$. In extreme ω-ω coupling, i.e., K = 0, we have $E = \pm\zeta_{np}$ and $C_2/C_1 = \pm 1$, eq.(3) gives the wave functions of $(1/2,1/2)_0$ and $(3/2,3/2)_0$ respectively. From this, we get eq.(2) and

$$\Psi^\circ(^1\Sigma_0^+) = -\frac{1}{\sqrt{2}}(1/2,1/2)_0 + \frac{1}{\sqrt{2}}(3/2,3/2)_0, \quad (5)$$

by a simple transformation. Thus, a and b in eq.(1) can be expressed in terms of C_1 and C_2 using eqs.(1),(2),(3), and (5), giving $a/b = (C_1-C_2)/(C_1+C_2)$. In calculating a/b, we estimated E in two different ways. One approach was to calculate E directly from K and ζ_{np}, where K was evaluated by approximating $\pi_g^{\pm}$ as linear combinations of Clementi and Roetti's double zeta valence of np atomic orbitals.[15] Alternatively, E was set equal to the splitting,[13] i.e., $2\lambda_0$, between $X^3\Sigma_0^-$ and $X^3\Sigma_1$ states, since this triplet splitting is predomiently due to the s-o interaction discussed above,[16] except perhaps in O_2.

In Table I, the results of the calculation are presented and compared with experiments, and Po_2 is also included for completeness. It is evident that the calculated K grossly overestimates the splitting between $^3\Sigma_g^-$ and $^1\Sigma_g^+$, since it is 2.66 in O_2 compared to 1.64 eV by experiment.[11] Therefore, it seems better to use the triplet splitting $2\lambda_0$ for E, and in fact, by doing this the calculation is brought closer to experiment for S_2 and Se_2. In Te_2, the probable cause of the disparity between calculation and experiment lies mainly in the uncertainty in the value of ζ_{np} or molecular s-o splitting. It therefore seems more appropriate to describe Te in the intermediate coupling scheme and extract ζ_{np} accordingly. When this ζ_{np} is used, the agreement with experiment is impressive, although ζ_{np} thus obtained for Te is actually larger than the s-o coupling constant in Te_2^+ (which is 0.47 eV).[4] In any event, considering the inherent approximations of the calculation, the agreement between experiments and calculations are generally very good; and this supports our interpretaion. It is predicted that in Po_2 the $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio will be even larger, to the extent the $^2\Pi_{3/2}$ state may be difficult to detect.

In the light of our discussion, it is evident that relativistic effects will have a similar influence on the intensity ratio of the s-o components in every molecule with open-shell, π^2 configuration and appreciable s-o interactions. This includes, for example, the heteronuclear Group VI, all heavy Group IV, and Group V-VII diatomic molecules. Furthermore, the present interpretation predicts, in the absence of cross section difference, $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratios of 1 for I_2, Bi_2, and for other closed shell molecules, as corroborated by experiment.[8,9]

The present case of intermediate coupling can be conveniently described pictorially. Fig. 1 shows the dependence of the intermediate coupling or a^2/b^2 upon the relative strengths of $\vec{\ell}\cdot\vec{s}$ interaction and exchange integral. Although the figure is drawn for dichalcogens, it can be generally applied to other open shell diatomics to estimate the $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio as long as the s-o and exchange splittings are known.

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Table I. Calculated and Experimental Branching Ratios of $^2\Pi_{g,1/2}/^2\Pi_{g,3/2}$ of Group VI Diatomics.

Molecule	ζ_{np}(eV)[a]	K(eV)	$E(XO_g^+)$(eV)[b]	C_2/C_1	a^2/b^2	$^2\Pi_{g,1/2}/^2\Pi_{g,3/2}$[c]	
O_2	0.0187	1.331	-1.31×10^{-4}	-7.02×10^{-3}	1.03	1.01	∿1.0[d]
	0.0187	—	-4.92×10^{-4}*	-2.63×10^{-2}	1.11	1.04	
S_2	0.0474	0.855	-1.31×10^{-3}	-2.77×10^{-2}	1.12	1.04	1.2[e]
	0.0474	—	-2.94×10^{-3}*	-6.19×10^{-2}	1.28	1.10	
Se_2	0.210	0.779	-2.78×10^{-2}	-0.132	1.70	1.38	∿2[f]
	0.240	0.779	-3.61×10^{-2}	-0.151	1.84	1.43	
	0.210	—	-4.55×10^{-2}*	-0.216	2.41	1.74	
	0.240	—	-4.55×10^{-2}*	-0.190	2.16	1.61	
Te_2	0.389	0.677	-0.104	-0.267	2.99	2.99	∿10[f]
	0.530	0.677	-0.183	-0.345	4.21	4.21	
	0.389	—	-0.276*	-0.711	35.0	35.0	
	0.530	—	-0.276*	-0.521	10.1	10.1	
Po_2[g]	1.688	0.586	-1.20	-0.711	35.2	35.2	—

(Continued)

Table I. Calculated and Experimental Branching Ratios of $^2\Pi_{g,1/2}/^2\Pi_{g,3/2}$ of Group VI Diatomics. (Continued)

a) Atomic s-o coupling contants estimated from optical data (Ref. 17); for O_2, S_2, and the first ζ_{np} value of Se_2 and Te_2, $\zeta_{np} = 2/3(^3P_0 - ^3P_2)$, while the second ζ_{np} value of Se_2 and Te_2, and that for Po_2 were obtained from extrapolation using ζ_{np} values of their respective neighboring atoms in the Periodic Table as given in Ref. 18. These latter ζ_{np}'s were obtained in the intermediate coupling scheme, which are more appropriate for the heavier atoms.

b) The energy given here is referenced to the unperturbed $X^3\Sigma_g^-$. The E values are from calculation (see text) and those denoted by stars are the splittings $2\lambda_0$ in $X^3\Sigma_g^-$ given in Ref. 13.

c) First column are calculated ratios by weighting a^2/b^2 appropriately by accounting for the thermal population of 1_g states (see text), i.e., $1_g/0_g^+ = 2\exp[E(0_g^+)/kT]$, and second column are experimental results. No such correction is necessary for Te_2 and Po_2.

d) Ref. 1 gives ∿0.95 and Ref. 2 ∿1.0 as estimated by present authors.

e) Estimated from Ref. 3 (Ref. 5 gives this estimated value as ∿1.5).

f) Ref. 4 and 5.

g) The MO of Te_2 with principal quantum number of atomic functions raised correspondingly by 1 was used for Po_2 to calculate K.

Figure Caption

Fig. 1 Schematic correlation between Λ-Σ (extreme left), intermediate and ω-ω coupling (extreme right) showing the dependence of a^2/b^2 upon the relative strengths of $\vec{\ell}\cdot\vec{s}$ (ζ_{np}) and exchange (K) interactions. The coupling cases of the individual dichalcogens are indicated explicitly with electrons denoted by bars.

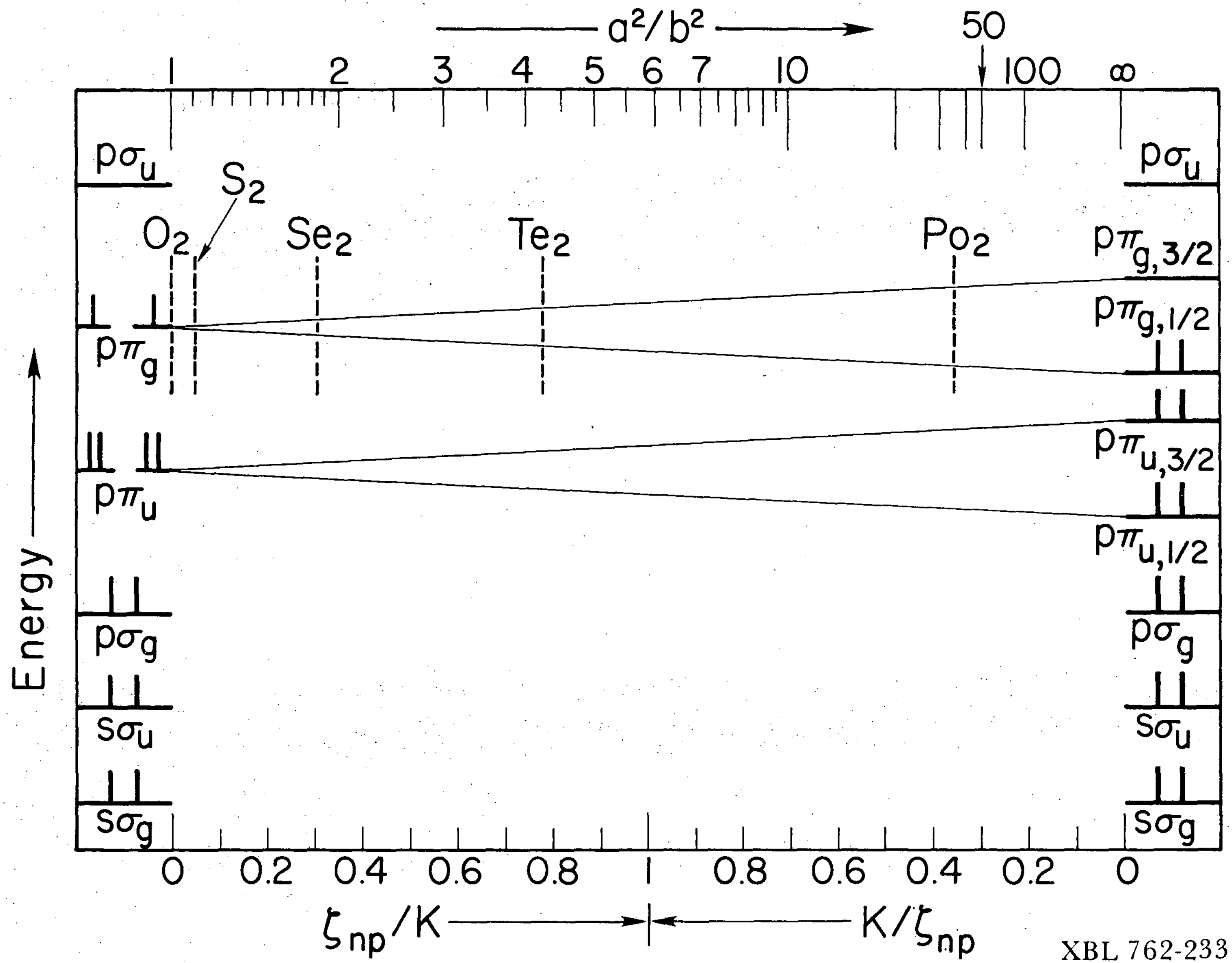

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Fig. 1

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