Lawrence Berkeley National Laboratory
Recent Work

Title
RELATIVISTIC EFFECTS IN THE UV PHOTOELECTRON SPECTRA OP GROUP VI DIATOMIC MOLECULES

Permalink
https://escholarship.org/uc/item/9jn171dh

Author
Lee, S.-T.

Publication Date
1976-02-01
RELATIVISTIC EFFECTS IN THE UV PHOTOELECTRON SPECTRA OF GROUP VI DIATOMIC MOLECULES

S.-T. Lee, Ş. Süzer, and D. A. Shirley

February 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Relativistic Effects in the UV Photoelectron Spectra of Group VI Diatomic Molecules

S.-T. Lee, S. Süzer, and D. A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

February 1976

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 \$35 in Po$_2$. 
The HeI photoelectron spectra of the group VI homonuclear diatomics, \( \text{O}_2, \text{S}_2, \text{Se}_2, \text{Te}_2 \) have all been reported. In every case, the spin-orbit (s-o) components of the \( \chi^2 \Pi_1^g \) ionic state were resolved. The branching ratio of \( \frac{2 \pi_{1/2}}{2 \pi_{3/2}} \) (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 \( \epsilon \pi \sigma \), rather than \( \epsilon \pi \pi \), channel. These additional constraints, together with the ground state of the heavier diatomic chalcogens being more appropriately described as \( \chi O_0^+ \), rather than \( \chi^3 \Sigma^-_g \) 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 \( \frac{2 \pi_{1/2}}{2 \pi_{3/2}} \) ratios in lighter diatomics than Te\(_2\) were attributed to contributions from the \( \chi^1 \) state, populated thermally because of smaller \( \chi^1 - \chi^0 \) splitting.

We note however, the above explanation is unsatisfactory if applied to other heavy linear molecules, where \( \Omega \) is more nearly a good quantum number in the ions and neutral molecules. The same arguments\(^4\)\(^5\) would then predict intensity ratios \( \frac{2 \pi_{1/2}}{2 \pi_{3/2}} \) 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,\textsuperscript{10} which caused the observed branching ratio of $^{2}\Pi_{1/2}/^{2}\Pi_{3/2}$ in Pb\textsuperscript{+} 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., $\Psi = a(p_{1/2})_{0}^{2} + b(p_{3/2})_{0}^{2}$, with $a^2/b^2 \approx 14$. 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.\textsuperscript{11,12} If only the electronic states are considered, this is identical to using $\omega-\omega$ rather than $\Lambda-\Sigma$ coupling,\textsuperscript{12} the molecular equivalents of j-j and L-S couplings respectively. In $\omega-\omega$ coupling, the $\hat{S}^{2}$ interaction splits the $\pi$ molecular orbital (MO) into $\omega = 1/2$ and 3/2 orbitals, with the former being lower in energy. For Group VI diatomics with the $\pi^{2}$ 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 $\Omega$, the axial projection of the total electronic angular momentum). The ground state of $\pi^{2}$ ($\Omega = 0$) can then be approximated in $\omega-\omega$ coupling by a simple CI
expansion

\[ \psi(XO^+_g) = a(1/2,1/2)_0 + b(3/2,3/2)_0. \]  

(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 \( \frac{2\pi_{1/2}}{2\pi_{3/2}} \) is given by \( a^2 / b^2 \). The relative weights of \( a \) and \( b \) depend on the strength of the \( \Lambda \cdot S \) interaction. In terms of \( \Lambda - \Sigma \) 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)

\[ \psi(3\Sigma^-_0 \text{ or } XO^+_g) = \frac{1}{\sqrt{2}} (1/2,1/2)_0 + \frac{1}{\sqrt{2}} (3/2,3/2)_0. \]  

(2)

and the \( \frac{2\pi_{1/2}}{2\pi_{3/2}} \) ratio is 1. By contrast, 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 \( O^+ \)) and \( X^3\Sigma^+_1 \) (or \( 1 \)) is not too large for the \( X\lambda g \) state to be populated thermally, but too small to be resolved, then the experimental ratio will be altered by contribution from \( X\lambda g \), which would give a \( \frac{2\pi_{1/2}}{2\pi_{3/2}} \) 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 \( \frac{2\Pi_{1/2}}{2\Pi_{3/2}} \) ratio theoretically. Because relativistic molecular wave functions are not available, we shall instead expand the nonrelativistic CI function in terms of \( \Lambda - \Sigma \) basis functions. Thus the ground state can be expressed as

\[ \psi(X^3\Sigma^-_{g,0} \text{ or } XO^+_g) = C_1 \psi(3\Sigma^-_0) + C_2 \psi(1\Sigma^+_0), \]  

(3)
\[
\psi^0(3\Sigma^+_0) = A \left[ \pi^+_g(1) \pi^-_g(2)(1/\sqrt{2})[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \times \text{[paired electrons]} \right]
\]

and

\[
\psi^0(1\Sigma^+_0) = A \left[ \pi^+_g(1) \pi^-_g(2)(1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times \text{[paired electrons]} \right].
\]

Approximating the s-o Hamiltonian by \( H_{s-o} = \rho_{ij}^s \rho_{ij}^o \), where \( \rho_{ij}^s \) is the atomic s-o coupling constant, we then obtain the matrix elements of \( H = H_o + H_{s-o} \) as follows:

\[
\begin{array}{ccc}
3\Sigma^-_0 & 1\Sigma^+_0 \\
3\Sigma^-_0 & E_o(3\Sigma^-_0) & \zeta_{np} \\
1\Sigma^+_0 & \zeta_{np} & E_o(1\Sigma^+_0),
\end{array}
\]

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 \( \pi^+_g \) and \( \pi^-_g \) 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 \( \omega-\omega \) 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

\[
\psi^0(1\Sigma^+_0) = \frac{1}{\sqrt{2}}(1/2,1/2)_0 + \frac{1}{\sqrt{2}}(3/2,3/2)_0,
\]

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 $\zeta_{np}$, where $K$ was evaluated by approximating $\pi^+$ as linear combinations of Clementi and Roetti's double zeta valence of np atomic orbitals. Alternatively, $E$ was set equal to the splitting, i.e., $2\lambda_0$, between $\chi^3\Sigma^+_0$ and $\chi^3\Sigma^-_1$ states, since this triplet splitting is predominantly due to the s-o interaction discussed above, 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. 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 $\zeta_{np}$ or molecular s-o splitting. It therefore seems more appropriate to describe $Te$ in the intermediate coupling scheme and extract $\zeta_{np}$ accordingly. When this $\zeta_{np}$ is used, the agreement with experiment is impressive, although $\zeta_{np}$ thus obtained for $Te$ is actually larger than the s-o coupling constant in $Te^+$ (which is 0.47 eV). In any event, considering the inherent approximations of the calculation, the agreement between experiments and calculations are generally very good; and this supports our interpretation. 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, $\pi^2$ 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, $\frac{2\Pi_{1/2}}{2\Pi_{3/2}}$ ratios of 1 for I₂, Bi₂, 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 $\hat{s}\cdot\hat{s}$ interaction and exchange integral. Although the figure is drawn for dichalcogens, it can be generally applied to other open shell diatomics to estimate the $\frac{2\Pi_{1/2}}{2\Pi_{3/2}}$ ratio as long as the s-o and exchange splittings are known.
ACKNOWLEDGEMENTS:

We wish to thank Professor K. Pitzer for a stimulating discussion, Mr. R. L. Martin for the use of his diatomic molecule computer program and Dr. J. Berkowitz for a copy of preprint of Ref. 5.

Work performed under the auspices of the Energy Research and Development Administration.
Footnotes and References.


9. S. Süzer, S.-T. Lee, and D. A. Shirley, to be published.


12. R. S. Mullikan, Phys. Rev. 46, 549 (1934); 57, 500 (1940).
Table I. Calculated and Experimental Branching Ratios of $^2\Pi_g,1/2$/$^2\Pi_g,3/2$ of Group VI Diatomics.

| Molecule | $\xi_{np}$ (eV)$^a$ | $K$ (eV) | $E(X^+_g)$ (eV)$^b$ | $C_2/C_1$ | $a^2/b^2$ | $^2\Pi_g,1/2$/$^2\Pi_g,3/2$  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>0.0187</td>
<td>1.331</td>
<td>$-1.31\times10^{-4}$</td>
<td>$-7.02\times10^{-3}$</td>
<td>1.03</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>0.0187</td>
<td>—</td>
<td>$-4.92\times10^{-4}$*</td>
<td>$-2.63\times10^{-2}$</td>
<td>1.11</td>
<td>1.04</td>
</tr>
<tr>
<td>$S_2$</td>
<td>0.0474</td>
<td>0.855</td>
<td>$-1.31\times10^{-3}$</td>
<td>$-2.77\times10^{-2}$</td>
<td>1.12</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>0.0474</td>
<td>—</td>
<td>$-2.94\times10^{-3}$*</td>
<td>$-6.19\times10^{-2}$</td>
<td>1.28</td>
<td>1.10</td>
</tr>
<tr>
<td>$Se_2$</td>
<td>0.210</td>
<td>0.779</td>
<td>$-2.78\times10^{-2}$</td>
<td>$-0.132$</td>
<td>1.70</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>0.240</td>
<td>0.779</td>
<td>$-3.61\times10^{-2}$</td>
<td>$-0.151$</td>
<td>1.84</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>0.210</td>
<td>—</td>
<td>$-4.55\times10^{-2}$*</td>
<td>$-0.216$</td>
<td>2.41</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>0.240</td>
<td>—</td>
<td>$-4.55\times10^{-2}$*</td>
<td>$-0.190$</td>
<td>2.16</td>
<td>1.61</td>
</tr>
<tr>
<td>$Te_2$</td>
<td>0.389</td>
<td>0.677</td>
<td>$-0.104$</td>
<td>$-0.267$</td>
<td>2.99</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>0.530</td>
<td>0.677</td>
<td>$-0.183$</td>
<td>$-0.345$</td>
<td>4.21</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>0.389</td>
<td>—</td>
<td>$-0.276$*</td>
<td>$-0.711$</td>
<td>35.0</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td>0.530</td>
<td>—</td>
<td>$-0.276$*</td>
<td>$-0.521$</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>$Po_2$</td>
<td>1.688</td>
<td>0.586</td>
<td>$-1.20$</td>
<td>$-0.711$</td>
<td>35.2</td>
<td>35.2</td>
</tr>
</tbody>
</table>

(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 constants estimated from optical data (Ref. 17); for O$_2$, S$_2$, and the first $\zeta_{np}$ value of Se$_2$ and Te$_2$, $\zeta_{np} = 2/3(3P_0 - 3P_2)$, while the second $\zeta_{np}$ value of Se$_2$ and Te$_2$, and that for Po$_2$ were obtained from extrapolation using $\zeta_{np}$ values of their respective neighboring atoms in the Periodic Table as given in Ref. 18. These latter $\zeta_{np}$'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 $X^3\Sigma^{-}$. The E values are from calculation (see text) and those denoted by stars are the splittings $2\chi_0$ in $X^3\Sigma^{-}$ 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., $l_g/O_g = 2\exp[E(O_g)/kT]$, and second column are experimental results. No such correction is necessary for Te$_2$ and Po$_2$.

d) Ref. 1 gives $\sim 0.95$ and Ref. 2 $\sim 1.0$ as estimated by present authors.

e) Estimated from Ref. 3 (Ref. 5 gives this estimated value as $\sim 1.5$).

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 $\vec{t} \cdot \vec{s}$ ($\epsilon_{np}$) and exchange (K) interactions. The coupling cases of the individual dichalcogenes are indicated explicitly with electrons denoted by bars.
Fig. 1