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Authors
Pitzer, K.S.
Balasubramanian, K.

Publication Date
1982-05-01
Materials & Molecular Research Division

Submitted to the Journal of Physical Chemistry

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May 1982

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Properties of Ten Electronic States of Pb₂ from Relativistic Quantum Calculations

Kenneth S. Pitzer and K. Balasubramanian
Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Abstract

Relativistic quantum mechanical calculations have been made for ten electronic states of Pb₂ as well as comparison calculations excluding the spin-orbit term. A recently developed ab initio method was used in which the spin-orbit effect is introduced at the configuration interaction step in the calculation. The results allow further interpretation of recent spectral data involving four states of Pb₂ and predict six additional states. The present results confirm all of the assumptions in a recent reinterpretation of the mass spectroscopic data for the dissociation energy of Pb₂ and agree well with that energy.

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Several recent spectroscopic investigations$^{1,2}$ of diatomic lead have
detected the presence of at least seven low-energy electronic states, but the
symmetry is clearly established for only three. Electron structure calcula-
tions were undertaken to determine the symmetries and other characteristics
of these states and the possible existence of other states in the same energy
range which have so far escaped experimental detection. The large relativistic
effects for Pb$^2+$ are also of theoretical interest. Adequate theoretical methods
have just been developed by Christiansen, Balasubramanian and Pitzer$^3$ and
applied to TlH where excellent agreement was obtained with the experimental
spectra. The same calculational program was used for Pb$^2+$.

Table I gives the molecular states which dissociate to atoms with total
energies up to 22000 cm$^{-1}$ above the lowest states $^3P_0 + ^3P_0$. Table II lists
the molecular orbital (MO) configurations expected to be low in energy with
the molecular terms first in $\Lambda$-$\Sigma$ (type a) coupling and then in $\omega$-$\omega$ (type c)
coupling which must be considered for Pb$^2+$. It is assumed that the 6s shells
are fully occupied; only the MO's derived from 6p orbitals are shown in
Table II. The $\sigma_g$ and $\pi_u$ orbitals are bonding; the $\pi_g$ orbitals are moderately
antibonding. The $\sigma_u$ orbitals are assumed to be so strongly antibonding that
they need be considered only for excitations / Even without including
any $\sigma_u$ or more than singly occupied $\pi_g$ orbitals, there are in all 23 single
electronic states and 36 doubly degenerate terms in $\omega$-$\omega$ coupling. We have
limited our calculations to those terms expected to be relatively low in
energy (within about 15000 cm$^{-1}$ of the lowest $0^+_g$ state). In all the energy
was calculated for 10 type c terms as listed in Table III; in addition calcu-
lations excluding the spin-orbit (SO) effect were made for three terms (then
described as type a).
The energy-distance curves are shown in Figure 1 for the \( g \) terms and in Figure 2 for the \( u \) terms with the lowest \( 0^+_g \) state shown in both.

One notes from Figure 1 that the SO effect greatly lowers the \( 0^+_g \) component state of \( {\Sigma}^-_g (\sigma^2g^2 \pi^2_u) \) in the range of the potential minimum. At shorter distances this \( 0^+_g \) state has an avoided crossing with the \( {\Sigma}^+_g (\pi^4_u) \) state (also \( 0^+_g \)) yielding a very peculiar curve with a marked shoulder in the repulsive side. The other component of \( {\Sigma}^-_g \), the \( 1^+_g \) term, is lowered less by the SO effect and has a normal shape of curve. Likewise the \( 2^+_g \) term (\( \Lambda^+_g \) in type a) is quite normal. The \( 1^+_g \) state (without SO) has a second minimum at longer distances; in this region it is primarily \( \sigma^2g^2 \pi^2_u \) rather than \( \pi^4_u \).

The \( 3\Pi_u \) term (without SO) splits to yield \( 2_u, 1_u, 0^-_u, \) and \( 0^+_u \) in increasing energy near their minima. But the \( 2_u \) term dissociates to higher energy atoms than \( 1_u \), hence the curves cross near 3.3 Å. The energy differences in these \( u \) terms can be understood best by considering first the \( \pi^3_u \) component which yields a lower \( 2\Pi_{3/2} \) term if a high-energy \( \pi_{3/2} \) spinor is vacant. If a lower energy \( \pi_{1/2} \) spinor is vacant, a higher energy \( 2\Pi_{1/2} \) term results. Then when the spin of the \( \sigma_g \) electron is coupled to the \( \pi_{3/2} \) group, there is a smaller splitting of the \( 2\Pi_{3/2} \) to \( 2_u \) and \( 1_u \) with \( 2_u \) lowest in agreement with Hund's third rule. From the \( 2\Pi_{1/2} \) term for \( \pi^3_u \) there arise the \( 0^-_u \) and \( 0^+_u \) terms in the energy sequence of their dissociation energies and the second \( 1_u \) term which relates to \( 1\Pi_u \) in type a coupling.

The SO effect causes large changes in dissociation energies. The ground \( 0^+_g \) state is only about half as strongly bound as the \( {\Sigma}^-_g \) state without SO. Among the states arising from \( 3\Pi_u \) on introduction of the SO term, the dissociation energy of \( 2_u \) is almost unchanged whereas that for \( 0^-_u \) is greatly reduced.
The calculated spectroscopic properties for the ten terms are given in Table III together with experimental values where available. The calculated \( R_e \) and \( \omega_e \) values are uncertain by a few hundredths of an \( \text{A} \) and by about 10 \( \text{cm}^{-1} \) respectively. By far the strongest absorption (near 19800 \( \text{cm}^{-1} \)) is to the second \( 0_u^+ \) or \( F \) state. This is expected since it is a simple one-electron \( \pi_u \) to \( \pi \) change. An energy curve for this state has been added to Figure 2 at the experimental energy but estimated as to \( R_e \). Since this state arises primarily from the configuration \( \sigma_g^2 \pi_u \pi_g \) it is expected to have a larger \( R_e \) than that for \( \sigma_g^2 \pi_u^2 \) and this is in agreement with the red shading of the experimental bands\(^1\). The transition probability from \( 0_g^+ \) to the lower \( 0_u^+ \) state is much smaller, in agreement with the nature of these states, and the calculated properties agree reasonably well with those measured, in particular the large anharmonicity and low dissociation energy. Also the calculated \( R_e \) value for the lowest \( 0_u^+ \) is smaller than that for \( 0_g^+ \) in agreement with the blue shading of the bands\(^1\).

Bondybey and English\(^1\) interpret a set of emission bands for \( \text{Pb}_2 \) in an inert matrix as arising by internal conversion from the \( F \) state to the long-lived \( B \) state at 12457 \( \text{cm}^{-1} \). This state is not connected to the ground state by a dipole-allowed transition but does radiate slowly because of matrix distortion or higher-order effects. Our calculations indicate this to be the \( 0_u^- \) state. Bondybey and English suggested the \( 2_u^2 \) state, but its energy is much too low from our calculations.

Matrix spectra also show emission bands near 13400 \( \text{cm}^{-1} \) connecting two new states. Since the upper or \( D \) state arises by internal conversion from the \( F \) state, the lower or \( A \) state cannot be more than 6540 \( \text{cm}^{-1} \) above the ground state. The most probable assignment for the \( A \) state is \( 1_g \) which we calculate at 4150 \( \text{cm}^{-1} \). The \( 2_u \) state cannot be absolutely eliminated since
our calculated energy of 6670 cm\(^{-1}\) might be in error by several hundred cm\(^{-1}\).

The calculated vibration frequency of the \(1\_g\) term agrees quite well, but again the \(2\_u\) term cannot be eliminated on that basis. The \(D\) state at an energy near 17500 cm\(^{-1}\) (or 19800 cm\(^{-1}\) if the \(A\) state is \(2\_u\)) is above the range for which we have reliable calculations. There are a multitude of \(g\) states from \(\sigma^2 \pi^2 g\) or \(u\) states from \(\sigma^2 \pi \pi^1 g\) or \(\pi^3 \pi^1 g\) some of which can be expected to have appropriate symmetry and to lie in this energy range.

The situation is similar for "E-A" emission bands near 14500 cm\(^{-1}\) observed only for a neon matrix by Teichman and Nixon\(^2\). The absence of these bands for argon or other matrices is puzzling. In this case the lower state must be the \(1\_g\) state.

There should be a dipole allowed \(1\_u \leftrightarrow 0\_g^+\) transition in the infrared near 7600 cm\(^{-1}\); this region should be investigated.

Our present calculations are less accurate for dissociation energy than for energy differences at bond distances. Hence it is probably somewhat accidental that our calculated dissociation energy for the \(0\_g^+\) state of \(0.88\) eV agrees almost exactly with the value of \(0.86 \pm 0.01\) eV from the mass-spectrometric data of Gingerich, et al.\(^4\) as reinterpreted by Pitzer\(^5\). The published interpretation of these data is further supported by the fact that the \(R_e\) value of 3.0 Å assumed for the partition function of \(\text{Pb}_2\) agrees very closely with our calculated value for the \(0\_g^+\) ground state. Also, none of the other states lie low enough to contribute appreciably to the partition function which confirms that assumption made in the reinterpretation.

We are making similar calculations for \(\text{Sn}_2\). Our calculated energy values at various interatomic distances and other details of the calculations for \(\text{Pb}_2\) will be given in a paper together with the corresponding results for \(\text{Sn}_2\).
Calculational Method

These calculations follow the same method as those of Christiansen, et al., for TlH; details and further references can be found in that paper. In brief, fully relativistic effective potentials (REP) are derived from numerical Dirac-Fock calculations for the lead atom. These REP are then averaged with respect to spin (AREP) and differenced to obtain \textit{ab initio} spin-orbit (SO) operators following Ermler, et al, and Hafner and Schwarz. Next a molecular SCF calculation is made in terms of the AREP (i.e., without the SO term) for each interatomic distance $R$ for the $^3\Sigma_g^-$ state. The orbitals from the SCF calculation are used for the spin-orbit, configuration-interaction treatment which yields the final results. In these final calculations selected single and double excitations are allowed from appropriate reference wave functions; also the SO terms are introduced.

A 14-electron atomic valence shell was used for the REP and SCF steps ($d^{10}s^2p^2$). All valence orbitals were freely optimized in the SCF calculation. Thereafter the d orbitals were frozen as fully occupied with excitation of the s and p electrons into the virtual space of d and s as well as p orbitals from the important reference configurations. Certain additional configurations important only near dissociation were included but without any excitations allowed.

A double zeta Slater basis was optimized for the $^3P$ atom. The zeta values were for d orbitals 3.5804 and 1.6047, for s orbitals 1.9021 and 0.8482, and for p orbitals 1.5189 and 0.8599.

A multiconfiguration treatment is needed even for the lead atom which is well-approximated neither in LS or jj coupling. Thus the ground state given as $^3P_0$ is actually a mixture of about 88% $^3P_0$ with 12% $^1S_0$. There is only one state with $J=1$, $^3P_1$, but for $J=2$ the $^3P_2$ and $^1D_2$ states are mixed. Good
agreement is obtained between calculated and experimental energies of these atomic terms. Likewise for Pb$_2$, the ground $^2\text{O}^+$ state involves significant components of $^2\text{O}^+$ symmetry from the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ terms from $\sigma_g^2\pi_u^2$ and the $^1\Sigma_g^+$ term from $\pi_u^4$, together with smaller components from the $^0\text{g}$ terms from $\sigma_g^2\pi_u^2$. Some of the excited states are simpler but a multiconfiguration treatment is still essential for accuracy. For the important reference configurations at bond distance an extensive and uniform pattern of excitations was included. Additional references important only near dissociation were added but without excitations. Since judgment is involved in this process, there is a subjective aspect in the final results, but we believe this aspect to be small.

Acknowledgment

This research was supported by the Director of the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U. S. Department of Energy through Contract DE-AC03-67SF00098.
References


Table I. The Molecular States of Pb\textsubscript{2} Related to Atoms
in Several Low-energy States and Their Energies in cm\textsuperscript{-1}. In Parenthesis is the Number of States of a Given Symmetry.

<table>
<thead>
<tr>
<th>dissociation limit</th>
<th>molecular states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3}!P_0 + ^3!P_0$ 0.0</td>
<td>$0^+ \ g$</td>
</tr>
<tr>
<td>$^{3}!P_0 + ^3!P_1$ 7819.4</td>
<td>$0^-, 0^-, 1_g, 1_u$</td>
</tr>
<tr>
<td>$^{3}!P_0 + ^3!P_2$ 10650.5</td>
<td>$0^+, 0^+, 1_g, 1_u, 2_g, 2_u$</td>
</tr>
<tr>
<td>$^{3}!P_1 + ^3!P_1$ 15638.7</td>
<td>$0^+ (2), 0^-, 1_g, 1_u, 2_g$</td>
</tr>
<tr>
<td>$^{3}!P_1 + ^3!P_2$ 18469.8</td>
<td>$0^+, 0^+, 0^-(2), 0^-(2), 1_g (3),$ $1_u (3), 2_g (2), 2_u (2), 3_g, 3_u$</td>
</tr>
<tr>
<td>$^{3}!P_2 + ^3!P_2$ 21300.9</td>
<td>$0^+ (3), 0^- (2), 1_g (2), 1_u (2),$ $2_g (2), 2_u, 3_g, 3_u, 4_g$</td>
</tr>
<tr>
<td>$^{3}!P_0 + ^1!D_2$ 21457.9</td>
<td>$0^+, 0^+, 1_g, 1_u, 2_g, 2_u$</td>
</tr>
</tbody>
</table>
Table II. A few MO Configurations and the Related Terms in Both
\(\Lambda-S\) and \(\omega-\omega\) Coupling

<table>
<thead>
<tr>
<th>(\sigma)</th>
<th>(g\pi u)</th>
<th>(3_g\mathbf{\Sigma}, 1_{\Delta}^g, 1_{\Sigma}^g)</th>
<th>(0_g^+, 1_g^+, 2_g^+, 0_g^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma)</td>
<td>(g\pi u)</td>
<td>(3_{\Pi}^g, 1_{\Pi}^g)</td>
<td>(0_u^+, 0_u^-, 1_u^-, 2_u^+, 1_u^+)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>(g\pi u)</td>
<td>(1_{\Sigma}^u)</td>
<td>(0_g^+)</td>
</tr>
<tr>
<td>(\pi)</td>
<td>(u)</td>
<td>(\left{\begin{array}{l}3_{\Delta}^u, 3_{\Sigma}^u, 3_{\Sigma}^u, 1_{\Delta}^u, \ 1_{\Sigma}^u, 1_{\Sigma}^u\end{array}\right}</td>
<td>(0_u^+(2), 0_u^-(2), 1_u(3)), (2_u(2), 3_u)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>(g\pi u)</td>
<td>(5_{\Pi}^g, 3_{\Phi}^g, 3_{\Pi}^g(4))</td>
<td>(0_g^+(5), 0_g^-(5), 1_g(9)), (2_g(6), 3_g(3), 4_g)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>(g\pi u)</td>
<td>(1_{\Phi}^g, 1_{\Pi}^g(3))</td>
<td>(2_g(6), 3_g(3), 4_g)</td>
</tr>
<tr>
<td>(\pi)</td>
<td>(u)</td>
<td>(\left{\begin{array}{l}3_{\Delta}^u, 3_{\Sigma}^u, 3_{\Sigma}^u, 1_{\Delta}^u, \ 1_{\Sigma}^u, 1_{\Sigma}^u\end{array}\right}</td>
<td>(0_u^+(2), 0_u^-(2), 1_u(3)), (2_u(2), 3_u)</td>
</tr>
</tbody>
</table>
Table III. Spectroscopic Parameters for Pb$_2$

<table>
<thead>
<tr>
<th>Term</th>
<th>$T_e$/cm$^{-1}$</th>
<th>$\omega_e$/cm$^{-1}$</th>
<th>$R_e$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc</td>
<td>exp</td>
<td>calc</td>
</tr>
<tr>
<td>X$^a$</td>
<td>0$^+_g$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>1$^+_g$</td>
<td>4150</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2$^u$</td>
<td>6670</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1$^u$</td>
<td>7570</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2$^g$</td>
<td>10130</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0$^+_u$</td>
<td>12920</td>
<td>12457</td>
</tr>
<tr>
<td></td>
<td>1$^g$(II)</td>
<td>13320</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0$^+_g$(II)</td>
<td>13640</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0$^+_u$</td>
<td>14130</td>
<td>15314</td>
</tr>
<tr>
<td></td>
<td>1$^u$(II)</td>
<td>15820</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The X, A, B, C labels are those of Bondybey and English.
Figure 1. Calculated potential curves for g states of Pb₂.
Figure 2. Calculated potential curves for u states and the ground 0^+ state of Pb_2. An estimated curve at the experimental T_e is also given for the upper 0_u^+ state.
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