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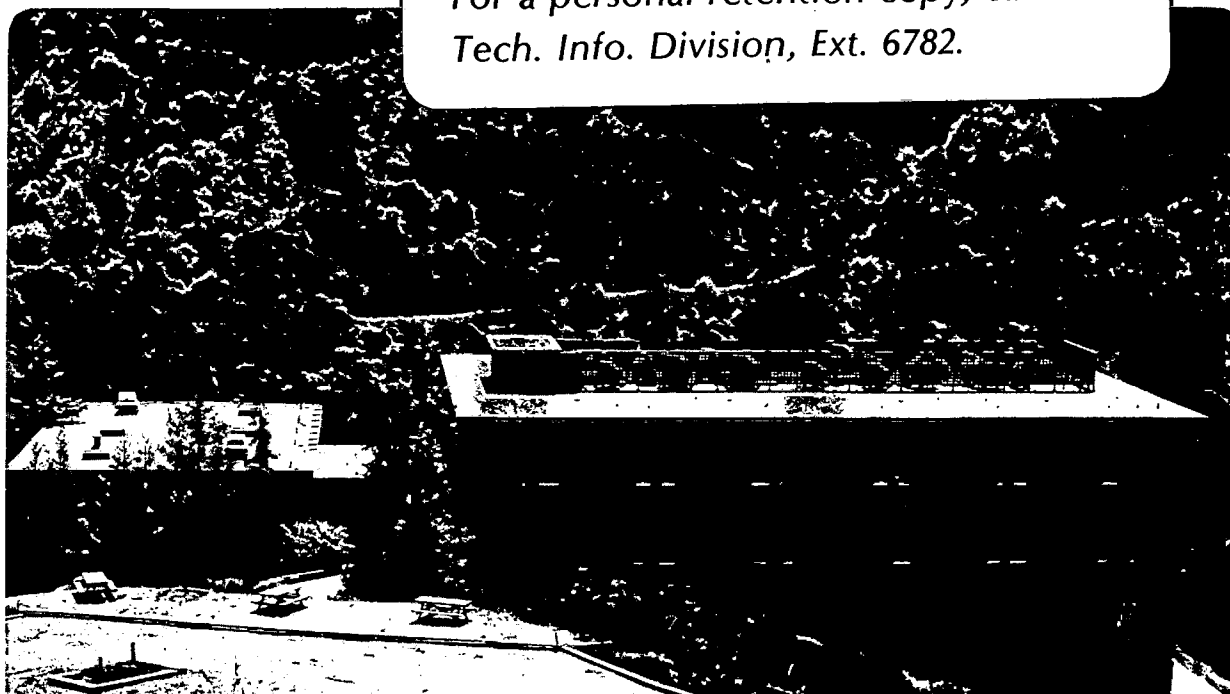
PROPERTIES OF TEN ELECTRONIC STATES OF Pb_2 FROM
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Kenneth S. Pitzer and K. Balasubramanian

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Properties of Ten Electronic States of Pb_2
from Relativistic Quantum Calculations

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Abstract

Relativistic quantum mechanical calculations have been made for ten electronic states of Pb_2 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 Pb_2 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 Pb_2 and agree well with that energy.

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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 calculations 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 Pitzer³ 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 $^3\text{P}_0 + ^3\text{P}_0$. Table II lists the molecular orbital (MO) configurations expected to be low in energy with the molecular terms first in Λ -S (type a) coupling and then in ω - ω (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 σ_g and π_u orbitals are bonding; the π_g orbitals are moderately antibonding. The σ_u orbitals are assumed to be so strongly antibonding that they need be considered only for excitations / in the CI calculation. Even without including any σ_u or more than singly occupied π_g orbitals, there are in all 23 single electronic states and 36 doubly degenerate terms in ω - ω 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 calculations 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 ${}^3\Sigma_g^- (\sigma_g^2 \pi_u^2)$ in the range of the potential minimum. At shorter distances this 0_g^+ state has an avoided crossing with the ${}^1\Sigma_g^+ (\pi_u^4)$ state (also 0_g^+) yielding a very peculiar curve with a marked shoulder in the repulsive side. The other component of ${}^3\Sigma_g^-$, the 1_g term, is lowered less by the SO effect and has a normal shape of curve. Likewise the 2_g term (${}^1\Delta_g$ in type a) is quite normal. The ${}^1\Sigma_g^+$ state (without SO) has a second minimum at longer distances; in this region it is primarily $\sigma_g^2 \pi_u^2$ rather than π_u^4 .

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 \AA . The energy differences in these u terms can be understood best by considering first the π_u^3 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 σ_g electron is coupled to the π_u^3 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 π_u^3 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 ${}^3\Sigma_g^-$ 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 ω_e values are uncertain by a few hundredths of an Å and by about 10 cm^{-1} , respectively. By far the strongest absorption (near 19800 cm^{-1}) is to the second O_u^+ or F state. This is expected since it is a simple one-electron π_u to π_g 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 bands¹. The transition probability from O_g^+ to the lower O_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 O_u^+ is smaller than that for O_g^+ in agreement with the blue shading of the bands¹.

Bondybey and English¹ interpret a set of emission bands for Pb_2 in an inert matrix as arising by internal conversion from the F state to the long-lived B state at 12457 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 O_u^- state. Bondybey and English suggested the 2_u state, but its energy is much too low from our calculations.

Matrix spectra also show emission bands near 13400 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 cm^{-1} above the ground state. The most probable assignment for the A state is 1_g which we calculate at 4150 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 $\sigma_g \pi_u^2 \pi_g$ or u states from $\sigma_g^2 \pi_u \pi_g$ or $\pi_u^3 \pi_g$ 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 $0.86 \pm .01 \text{ eV}$ 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 \AA assumed for the partition function of 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 Sn_2 . Our calculated energy values at various interatomic distances and other details of the calculations for Pb_2 will be given in a paper together with the corresponding results for Sn_2 .

Computational Method

These calculations follow the same method as those of Christiansen, et al.,³ 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 ab initio spin-orbit (SO) operators following Ermler, et al,⁶ and Hafner and Schwarz.⁷ 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 0_g^+ state involves significant components of 0_g^+ 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 π_u^4 , together with smaller components from the 0_g^+ terms from $\sigma_g \pi_u^2 \pi_g$. 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

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References

1. V. E. Bondybey and J. H. English, J. Chem. Phys., 67, 3405 (1977);
76, 2165 (1982).
2. R. A. Teichman III and E. R. Nixon, J. Mol. Spectr., 59, 299 (1976).
3. P. A. Christiansen, K. Balasubramanian, and K. S. Pitzer, J. Chem. Phys.,
in press.
4. K. A. Gingerich, D. L. Cooke, and F. Miller, J. Chem. Phys., 64, 4027
(1976).
5. K. S. Pitzer, J. Chem. Phys., 74, 3078 (1981).
6. W. C. Ermler, Y. S. Lee, P. A. Christiansen, and K. S. Pitzer,
Chem. Phys. Lett., 81, 70 (1981).
7. P. Hafner and W. H. E. Schwarz, Chem. Phys. Lett., 65, 537 (1979).

Table I. The Molecular States of Pb_2 Related to Atoms in Several Low-energy States and Their Energies in cm^{-1} . In Parenthesis is the Number of States of a Given Symmetry.

<u>dissociation limit</u>		<u>molecular states</u>
${}^3\text{P}_0 + {}^3\text{P}_0$	0.0	0_g^+
${}^3\text{P}_0 + {}^3\text{P}_1$	7819.4	$0_g^-, 0_u^-, 1_g, 1_u$
${}^3\text{P}_0 + {}^3\text{P}_2$	10650.5	$0_g^+, 0_u^+, 1_g, 1_u, 2_g, 2_u$
${}^3\text{P}_1 + {}^3\text{P}_1$	15638.7	$0_g^+(2), 0_u^-, 1_g, 1_u, 2_g$
${}^3\text{P}_1 + {}^3\text{P}_2$	18469.8	$\left\{ \begin{array}{l} 0_g^+, 0_u^+, 0_g^-(2), 0_u^-(2), 1_g(3), \\ 1_u(3), 2_g(2), 2_u(2), 3_g, 3_u \end{array} \right.$
${}^3\text{P}_2 + {}^3\text{P}_2$	21300.9	$\left\{ \begin{array}{l} 0_g^+(3), 0_u^-(2), 1_g(2), 1_u(2), \\ 2_g(2), 2_u, 3_g, 3_u, 4_g \end{array} \right.$
${}^3\text{P}_0 + {}^1\text{D}_2$	21457.9	$0_g^+, 0_u^+, 1_g, 1_u, 2_g, 2_u$

Table II. A few MO Configurations and the Related Terms in Both Λ -S and ω - ω Coupling

$\sigma_g^2 \pi_u^2$	$3_{\Sigma_g^-}, 1_{\Delta_g}, 1_{\Sigma_g^+}$	$0_g^+, 1_g, 2_g, 0_g^+$
$\sigma_g \pi_u^3$	$3_{\Pi_u}, 1_{\Pi_u}$	$0_u^+, 0_u^-, 1_u, 2_u, 1_u$
π_u^4	$1_{\Sigma_g^+}$	0_g^+
$\sigma_g^2 \pi_u \pi_g$	$\left\{ \begin{array}{l} 3_{\Delta_u}, 3_{\Sigma_u^+}, 3_{\Sigma_u^-}, 1_{\Delta_u}, \\ 1_{\Sigma_u^+}, 1_{\Sigma_u^-} \end{array} \right.$	$0_u^+(2), 0_u^-(2), 1_u(3),$ $2_u(2), 3_u$
$\sigma_g \pi_u^2 \pi_g$	$\left\{ \begin{array}{l} 5_{\Pi_g}, 3_{\phi_g}, 3_{\Pi_g}(4), \\ 1_{\phi_g}, 1_{\Pi_g}(3) \end{array} \right.$	$0_g^+(5), 0_g^-(5), 1_g(9),$ $2_g(6), 3_g(3), 4_g$
$\pi_u^3 \pi_g$	$\left\{ \begin{array}{l} 3_{\Delta_u}, 3_{\Sigma_u^+}, 3_{\Sigma_u^-}, 1_{\Delta_u}, \\ 1_{\Sigma_u^+}, 1_{\Sigma_u^-} \end{array} \right.$	$0_u^+(2), 0_u^-(2), 1_u(3),$ $2_u(2), 3_u$

Table III. Spectroscopic Parameters for Pb_2

Term	T_e/cm^{-1}		ω_e/cm^{-1}		$R_e/\text{\AA}$
	calc	exp	calc	exp	calc
X ^a 0_g^+	0	0	103	110	2.9 ₇
A 1_g	4150	-	124	122	2.9 ₄
- 2_u	6670	-	119	-	2.7 ₀
- 1_u	7570	-	119	-	2.7 ₁
- 2_g	10130	-	105	-	3.0 ₃
B 0_u^-	12920	12457	106	-	2.7 ₅
- $1_g(\text{II})$	13320	-	100	-	3.0 ₇
- $0_g^+(\text{II})$	13640	-	74	-	3.1 ₈
C 0_u^+	14130	15314	115	129	2.7 ₄
- $1_u(\text{II})$	15820	-	123	-	2.7 ₃

^a The X, A, B, C labels are those of Bondybey and English.¹

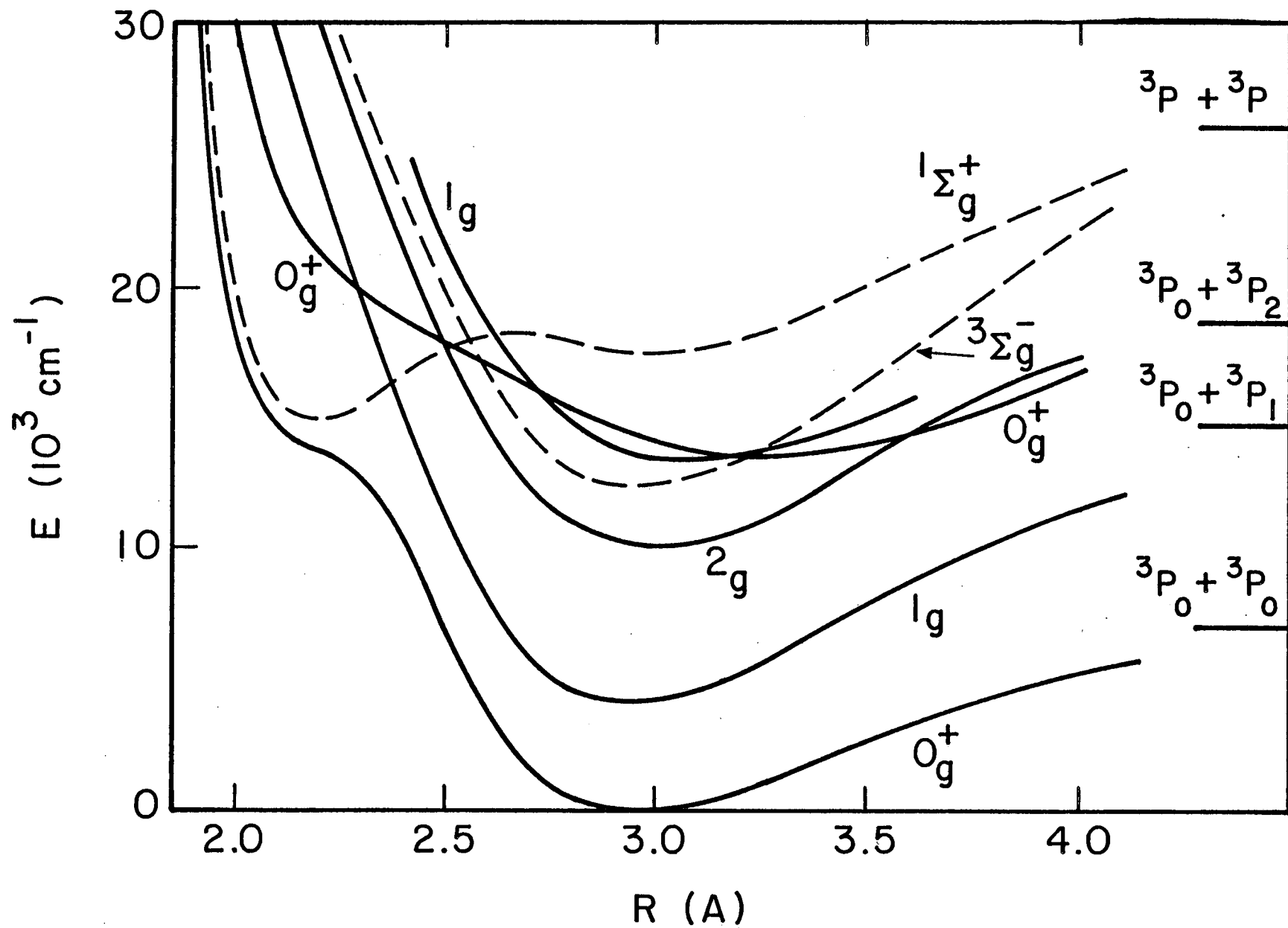


Figure 1. Calculated potential curves for g states of Pb_2 .

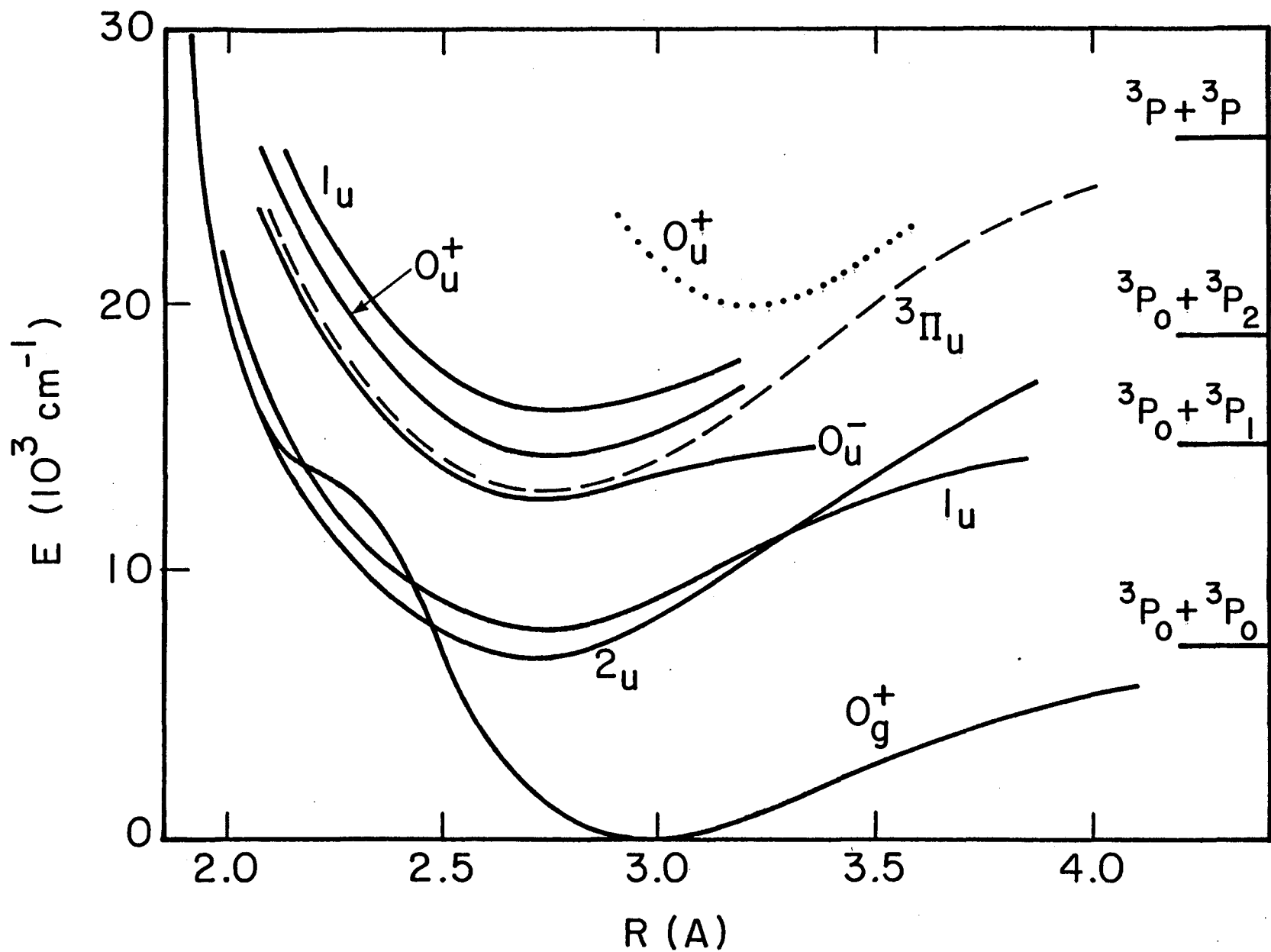


Figure 2. Calculated potential curves for u states and the ground 0_g^+ state of Pb_2 . An estimated curve at the experimental T_e is also given for 0_u^+ the upper 0_u^+ state.

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