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July 1982

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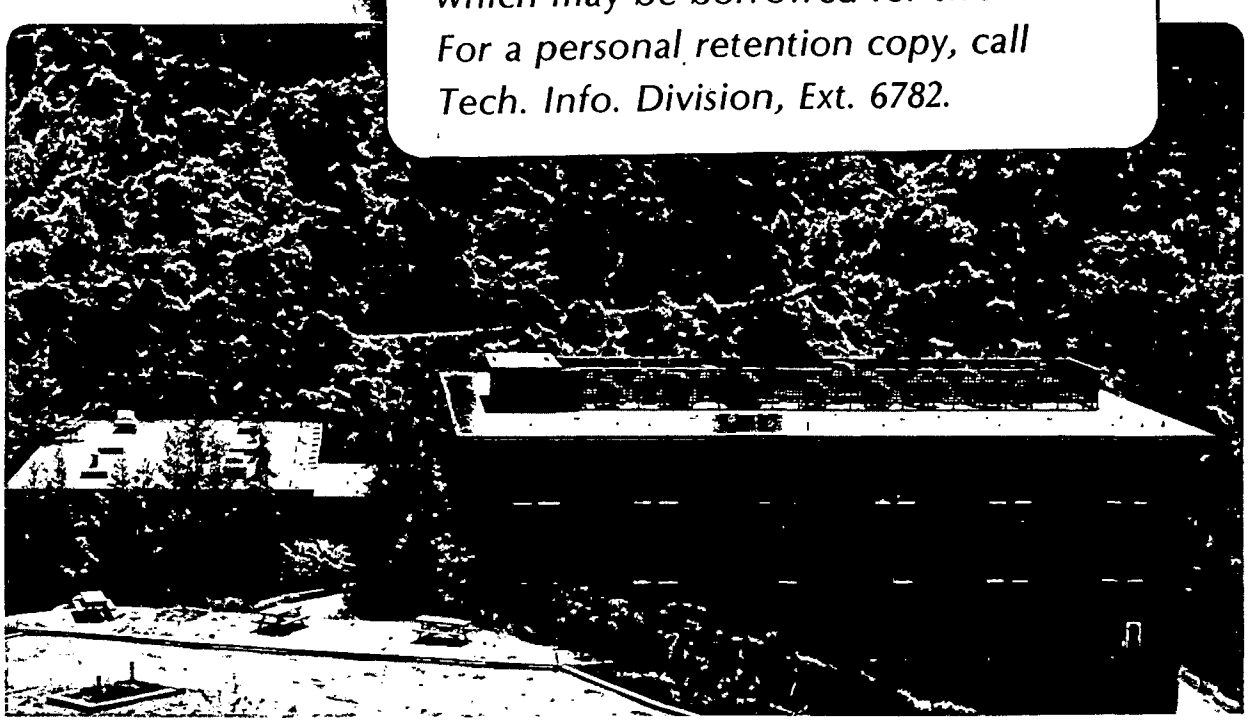

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Electron Structure Calculations Including CI for Ten Low Lying States of Pb_2 and Sn_2. Partition Function and Dissociation Energy of Sn_2

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(Abstract)

Relativistic calculations including configuration interaction are described for 10 low lying states of Pb_2 and Sn_2. These calculations were accomplished by introducing spin-orbit interaction at the configuration interaction stage in calculations initiated in Λ-S coupling. All the calculations were carried out with relativistic effective potentials which were averaged with respect to spin at SCF stage and differenced for the spin-orbit operator. The selection of important configurations for the atoms and the molecules is discussed in terms of both Λ-S and ω-ω coupling. Comparisons are made with the available experimental data. With the results of these calculations and recent experimental spectra, it is possible to revise the partition function for Sn_2. The partition function is required for the interpretation of mass spectral data on the dissociation energy. The optimum method for the calculation of the partition function where several electronic states are populated is discussed in general terms and then applied to the revision of the dissociation energy of Sn_2 with the result 2.04 ± 0.1 eV. An earlier revision for Pb_2 needs no further change.

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I. Introduction

Methods for relativistic electron structure calculations for molecules have recently been extended to allow a high order configuration interaction (CI) treatment yielding accurate values of energies and other properties. The first application was to the molecule TℓH which was chosen because of the large spin-orbit (SO) effect for the 6p electron. A general description of the calculational method was given in the paper[1] on TℓH and in a review[2]; hence it will not be repeated here.

In this paper the calculational method is applied to the somewhat more complex molecules Sn_2 and Pb_2. These molecules have eight valence-level s and p electrons in contrast to the four in TℓH. The SO effect is much larger for Pb than for Sn; hence a comparison of the results is of considerable interest from that viewpoint. The spectra of these molecules are now being actively investigated.[3-8] Our results for the excited states confirm some spectral interpretations and suggest some new assignments. This aspect was discussed in a preliminary presentation[9] of the results for Pb_2.

The possibility of excited electronic states contributing substantially to the molecular partition function is widely recognized, but the examples presented are often simplified cases where the moment of inertia and the vibration frequency of each excited state remain essentially equal to the values for the ground state. For Sn_2 there are several excited electronic states that are appreciably populated at the temperature of the dissociation energy measurements (1600 K), and the moments of inertia and vibration frequencies differ substantially from state to state. The appropriate equations are reviewed

and values are then calculated for the partition function. These values are used to revise the interpretation of the heat of dissociation measurements[10,11] of Sn_2. The case of Pb_2 is somewhat simpler from this viewpoint and a previous revision[12] of the dissociation energy interpretation for that molecule needs no further change.

II. Quantum Mechanical Calculations

Before discussing the details of the calculations the symmetry relationships and dissociation limits should be noted. The dissociation relationships in ω-ω coupling are given in Table I with the energies of the atoms for both tin and lead. Table II gives a few molecular orbital configurations and the related terms first in Λ-S coupling and then the ω-ω states into which these are split by the spin-orbit effect.

We next note that a multiple configuration treatment is required for even an adequate zero-order treatment of the lead atom which is said to be in intermediate coupling, i.e., neither L-S nor j-j coupling offers a good approximation in a single configuration. The tin atom is much closer to L-S coupling, but the spin-orbit effect is still substantial as is indicated in Table I. This is in contrast to the situation for thallium where the $^2P_{1/2}$ and $^2P_{3/2}$ states are each described by single j-j configurations. We discuss first the atom and then the Pb_2 molecule in terms of both L-S (Λ-S) and j-j (ω-ω) coupling.

Atomic wavefunctions in L-S coupling are presented in various sources.[13] For p^2 one finds the terms $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, and $^1S_0$. There is but one $J=1$ state. But for $J=0$ the real states are mixtures of $^3P_0$ and $^1S_0$ while for $J=2$ the $^3P_2$ and $^1D_2$ mix to form the real states. The development in j-j coupling is less familiar and will be described briefly.

An atomic p spinor with j = 1/2, m = 1/2 may be written in several ways

$$(1/2)^{1/2} = \binom{\sigma}{\pi^+} = \binom{\sigma}{0} + \binom{0}{\pi^+} = \sigma\alpha + \pi^+\beta = \sigma\alpha + x\beta + iy\beta \qquad (1)$$

where the superscript on π indicates the + or - sign of m_ℓ; only the large components of the Dirac spinors are included; quantitative coefficients are omitted; and the α and β have their usual significance for spin. After the last equality the expansion into real cartesian functions is indicated where the x and y are abbreviations for π_x and π_y, respectively. With the omission of some intermediate steps, the complete set of p spinors (with j in parentheses and m the superscript) follows:

$$(1/2)^{1/2} = \binom{\sigma}{\pi^+} = \sigma\alpha + \pi^+\beta = \sigma\alpha + x\beta + iy\beta \qquad (2a)$$

$$(1/2)^{-1/2} = \binom{\pi^-}{-\sigma} = -\sigma\beta + \pi^-\alpha = -\sigma\beta + x\alpha - iy\alpha \qquad (2b)$$

$$(3/2)^{1/2} = \binom{\sigma}{-\pi^+} = \sigma\alpha - \pi^+\beta = \sigma\alpha - x\beta - iy\beta \qquad (2c)$$

$$(3/2)^{-1/2} = \binom{\pi^-}{\sigma} = \sigma\beta + \pi^-\alpha = \sigma\beta + x\alpha - iy\alpha \qquad (2d)$$

$$(3/2)^{3/2} = \binom{\pi^+}{0} = \pi^+\alpha = x\alpha + iy\alpha \qquad (2e)$$

$$(3/2)^{-3/2} = \binom{0}{\pi^-} = \pi^-\beta = x\beta - iy\beta. \qquad (2f)$$

There are differences in sign conventions for the terms in these spinors in various books and papers. We need not be concerned with these details since we shall always determine signs from symmetry and then optimize the coefficients. Note that the $(1/2)^{1/2}$ and $(3/2)^{1/2}$ spinors differ only in the signs and quantitative coefficients. Thus, if these coefficients are optimized, there is no need to consider configurations differing only by the change of these m = 1/2 spinors or of the corresponding -1/2 spinors.

We take the case J = 2 as an example. The wavefunction for M = +2 is

$$(3/2)^{3/2}(1/2)^{1/2} + (3/2)^{3/2}(3/2)^{1/2} = \pi^{+}\alpha(c_1\sigma\alpha + c_2\pi^{+}\beta)$$

$$= c_1\pi^{+}\alpha\sigma\alpha + c_2\pi^{+}\alpha\pi^{+}\beta. \qquad (3)$$

In this case the first term is clearly from a triplet, hence from $^3P_2$, while the second is a singlet with L = +2 and hence is from $^1D_2$. For our calculations the further expansion into cartesian orbitals yields

$$c_1(x\alpha\sigma\alpha + iy\alpha\sigma\alpha) + c_2(x\alpha x\beta - y\alpha y\beta + ix\alpha y\beta + iy\alpha x\beta)$$

For the lowest J = 2 state we find for lead $c_1/c_2 = 2.1$ which corresponds to 70% $^3P_2$ and 30% $^1D_2$. We find that tin is 97% $^3P_2$ and only 3% $^1D_2$.

As noted above the J = 1 state is unambiguously $^3P_1$ but there are again two J = 0 states. Since there are in all five M = 0 wavefunctions, the analysis for J = 0 is more complex, but one finds eventually that the lowest J = 0 state in lead is 88% $^3P_0$ and 12% $^1S_0$ and in tin is 97% $^3P_0$ and 3% $^1S_0$. It is customary to use the symbols $^3P_0$ and $^3P_2$ for the lowest J = 0 and 2 atomic states even though they are mixed.

Our effective potential calculations yield the following energy differences for the atoms: 7725 and 11740 cm^{-1} for the $^3P_1$ and $^3P_2$ states in Pb and 1970 and 3950 cm^{-1} for Sn, respectively. These agree reasonably well with the experimental values in Table I.

In j-j coupling the lowest J = 0 state has a closed shell structure with both j = 1/2 spinors occupied

$$(1/2)^{1/2}(1/2)^{-1/2} = \binom{\sigma}{\pi^{+}}\binom{\pi^{-}}{\sigma}$$

$$= \sigma\alpha\sigma\beta + \sigma\alpha\pi^{-}\alpha + \sigma\beta\pi^{+}\beta + \pi^{-}\alpha\pi^{+}\beta. \qquad (4)$$

This expands into 9 terms on the cartesian basis. The cartesian expansion for the other $M = 0$ states in j-j coupling yield these same 9 terms in various combinations. Thus no new cartesian terms are needed for a full treatment of the lowest $J = 0$ state in intermediate coupling.

For the diatomic molecule in Λ-S coupling Table II lists several configurations and the corresponding Λ-S terms. Also given are the ω-ω terms into which these Λ-S terms expand. Included are the configurations with only bonding orbitals occupied and those involving one promotion to an antibonding π_g orbital. The σ_u orbital is, presumably, much more strongly antibonding; configurations occupying σ_u are unlikely to be important at bond distances for low-energy states, but they must be introduced at the CI stage for dissociation or for electron correlation.

The selection of configurations for inclusion in the CI calculations is rather complicated. With four valence p electrons outside the completed d and s shells one could formulate just a complete array of configurations based on promotions within the p orbitals. Correlation of the valence shell s electrons, however, is significant, and our calculational program did not permit a complete coverage of all possible excitations for the eight electron system. We chose a system which included an extensive array of single and double excitations from the higher-energy, antibonding $s\sigma_u$ orbital as well any of the p orbitals in a set of important "reference configurations". This set included all configurations occupying only bonding p orbitals and those other configurations in Table II which were found to have significant coefficients in test calculations at the bond distance. The numbers of these important reference configurations in cartesian form for each molecular state are listed in the column marked "RC" in Table III together with the total number of configurations, including excitations, in each case. In addition

to the appropriate single and double excitations from these reference configurations, a number of additional configurations, including a considerable number with quadruple excitations, were included to allow dissociation to neutral atoms. For the lowest 0_g^+ state dissociating to two ground-state atoms, we are confident that this list of additional configurations is complete; this aspect will be discussed below in terms of ω-ω coupling. For other molecular states dissociating to atoms in different states, usually in intermediate coupling, this problem is more complex, and we now believe that our lists of additional configurations are probably incomplete. Thus the calculated energies are meaningful at 9 bohr only for 0_g^+ and even at 7 bohr they are probably too high for several states. We do not believe this limitation is significant at 6 bohr or shorter distances. If it should become important to determine the exact level of the potential curves near dissociation, new calculations should be made with more extended arrays of excited configurations. These near-dissociation details did not appear to be of sufficient current interest to justify a new set of more elaborate calculations; consequently the potential curves were drawn smoothly toward the known energies of the dissociated atoms.

On the cartesian basis the configurations for 2_g all appear in the list for 0_g^+, although 0_g^+ includes some additional configurations. We did not determine exactly how many of the 0_g^+ configurations are eliminated by symmetry from the 2_g, but it is a rather small fraction. The same situation applies for the 2_u, 0_u^+, and 0_u^- states. The cartesian configurations for 0_u^+ and 0_u^- are identical (but some coefficients differ in sign). For 2_u we did eliminate the inappropriate configurations on the 0_u^+ list and the smaller numbers for 2_u appear in Table III.

The general treatment for the molecule becomes more complex in ω-ω coupling, but there are some advantages in that approach, nevertheless. Only the 0_g^+ state will be discussed in detail.

Diatomic molecular spinors are formed by sum and difference combinations of the atomic spinors. With the same abbreviated symbols defined above there are four molecular spinors based on the low-energy $p_{1/2}$ atomic spinors. The u-g symmetry is now shown as a subscript. One has

$$(1/2)_g^{1/2} = \begin{pmatrix} \sigma_g \\ \pi_g^+ \end{pmatrix} = \sigma_g\alpha + \pi_g^+\beta \tag{5a}$$

$$(1/2)_g^{-1/2} = \begin{pmatrix} \pi_g^- \\ -\sigma_g \end{pmatrix} = -\sigma_g\beta + \pi_g^-\alpha \tag{5b}$$

and similarly for the ungerade spinors. $\sigma_g\alpha$, $\pi_g^+\beta$, etc. are now molecular spin-orbitals.

The most important configuration for the lowest 0_g^+ state simply occupies these four molecular spinors that are based on $p_{1/2}$ atomic spinors.

$$(1/2)_g^{1/2}(1/2)_g^{-1/2}(1/2)_u^{1/2}(1/2)_u^{-1/2}$$

$$= (\sigma_g\alpha + \pi_g^+\beta)(-\sigma_g\beta + \pi_g^-\alpha)(\sigma_u\alpha + \pi_u^+\beta)(-\sigma_u\beta + \pi_u^-\alpha). \tag{6}$$

This product of molecular spinors evidently expands into 16 products of spin-orbitals. These sixteen terms include all of those of 0_g^+ symmetry arising from $\sigma_g^2\pi_u^2$ in Table II. Expansion of the 16 terms to the cartesian basis yields 81 configurations. All of these were included, 20 as reference configurations with multiple excitations also included and 61 as single configurations. The spinor product, equation (6), is equivalent

to a product of $p_{1/2}$ spinors for each of the two atoms; hence, this function dissociates to neutral atoms in their lowest spinor configurations.

Furthermore, it was noted above that the 9 cartesian terms arising from the product of $p_{1/2}$ atomic spinors, equation (4), contain all of the terms needed for intermediate coupling for the lowest atomic state. Thus the 81 cartesian configurations for the molecule allow dissociation to the atoms in their state of intermediate coupling.

Spinor products involving one or more $p_{3/2}$ spinors can be written which include, among their spin-orbital product terms, the other configurations included in the 0_g^+ calculation. The treatment of other states could also be discussed in terms of spinor products. These details, however, would add little to the information already included in Table III and the discussion on a spin-orbital, Λ-S coupling basis.

The calculations were carried out with a fourteen electron $d^{10}s^2p^2$ valence shell. The effective potentials were generated from Dirac-Fock atomic calculations for the ground state and for appropriate excited states.

For the molecular calculations a double-zeta Slater-type basis was used. The orbital exponents were optimized for the ground ^3P state of each atom in LS coupling with spin-averaged EP. These orbital exponents are given in Table IV.

SCF calculations with spin-averaged EP were the first stage of the molecular treatment. The orbitals and integrals from this step were used for the CI stage wherein spin-orbit terms were included as well as electron repulsion terms.

III. Results and Comparisons with Electronic Spectra

The calculated energies in hartrees are listed as a function of interatomic distance in bohr for Pb_2 in Table V and for Sn_2 in Table VI. In each case the zero of energy is the minimum for the ground 0_g^+ state. Values are also given for three states without the spin-orbit term. The spectroscopic constants for these states are given in Table VII

The potential energy curves for Pb_2, based on these calculated energies, are shown in Figures 1 and 2 while the corresponding curves for Sn_2 are in Figures 3 and 4. As noted above, we believe our lists of configurations, although adequate near the potential minimum, were inadequate to give the full dissociation curve except for the ground 0_g^+ state. Thus the curves in Figures 1-4 for other states were drawn smoothly toward the energies of the dissociated atoms and in some cases deviate from the calculated values in Tables V and VI at the largest R values. The calculated dissociation energies of the ground states, based on the values at 11 bohr for Pb_2 and at 10 bohr for Sn_2, will be compared with revised experimental values in section IV.

The fractional populations of various Λ-S molecular configurations in the ground states are shown in Figure 5. In each case the π_u^4 configuration dominates at very short distances (less than R_e). There is a sudden shift in Sn_2 to the $\sigma_g^2\pi_u^2$ configuration which dominates for R greater than 4.4 bohr. The $^3\Sigma_g^-$ component of $\sigma_g^2\pi_u^2$ predominates with only a small contribution from the $^1\Sigma_g^+$ component. The $\sigma_g\pi_g\pi_u^2$ configuration gradually becomes more important with increasing R.

For Pb_2 the qualitative pattern is the same but the relative contribution is much larger for the $\sigma_g\pi_g\pi_u^2$ configuration and the $^1\Sigma_g^+$ component of $\sigma_g^2\pi_u^2$. This is expected since the mixing of the $^1\Sigma_g^+$ and $^3\Sigma_g^-$ components arises from the spin orbit effect.

The potential curves for the ground 0_g^+ state show the shift from π_u^4 to other configurations. For Pb_2 there is a marked shoulder on the repulsive side of the curve. For Sn_2 it is a more subtle effect but still apparent. Without SO the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ curves do not interact but rather cross one another in this region.

The relation of these results to the rather extensive experimental spectra[3,4] for Pb_2 was discussed in the earlier publication.[9] The experimental information[5-8] for Sn_2 is less extensive. The vibration frequency of the ground state is well established as 188 cm^{-1} in rare gas matrices[7,8] and 190 cm^{-1} in the gas.[5] The calculated value 197 cm^{-1} agrees well within the estimated uncertainty of about 10 cm^{-1} for the calculated frequencies.

Most of the excited electronic states that have been observed in Sn_2 lie far above the 10000 cm^{-1} level of the highest state among those calculated. The lowest 0_u^+ state in Pb_2 was calculated at 14130 cm^{-1} in reasonable agreement with the measured 15314 cm^{-1} level. The corresponding state in Sn_2 is at 4192 cm^{-1}; this frequency range may not have been investigated.

The strongest absorption in Pb_2 is to a second 0_u^+ state at 19800 cm^{-1} which presumably corresponds to the 0_u^+ state reported[5] for Sn_2 at 18223 cm^{-1}. An emission in the 12000-14000 cm^{-1} range for Sn_2 has been interpreted[6] as leading to a state about 3000-5000 cm^{-1} above the ground state with a harmonic vibration frequency about 195 cm^{-1}. Both the 0_u^+ and 0_u^- states near 4100 cm^{-1} fit the first criterion and the 1_u state at 2500 cm^{-1} is probably close enough to be considered. These are all components of the $^3\Pi_u$ term in Λ-S coupling. Their calculated vibration frequencies are a bit too high , near 220 cm^{-1}. Since these bands are relatively broad and both the vibrational assignment and the anharmonicity are uncertain, there is little further to be said at this time about the discrepancy in vibration frequencies. Indeed it is

possible that this array of bands contains contributions from more than one transition involving the 0_u^+, 0_u^-, or 1_u states.

These various considerations of the low-lying excited states of Sn_2 indicate the need for a thorough investigation for both absorption and fluorescence in the infrared region.

IV. Dissociation Energy

The dissociation energies of both Pb_2 and Sn_2 have been measured by mass spectrometry. The "third-law" method of interpretation of the results requires knowledge of the partition functions for each molecule and the dissociated atoms. The atomic properties are well-known, but molecular properties were estimated in each case. Recent spectroscopic measurements[3-8] provide vibration frequencies with which our present calculations agree. Our calculations also provide bond distance values and the energies and other properties of excited states. These data allow calculation of improved values of the partition function for the diatomic molecules. This process was carried out earlier[12] for Pb_2 and the revised energy of dissociation of 0.86 ± 0.01 eV agrees very well with our calculated value of 0.88 eV.

For Pb_2 the excited electronic states are at too high an energy to contribute appreciably, hence the calculation is quite simple. For Sn_2, however, the 1_g, 2_u, and 1_u states are all at low enough energy that they need to be included at the temperature of mass spectrometric measurement[10,11] near 1600 K. Furthermore the values of R_e and ω_e for these states differ appreciably from the corresponding values for the 0_g^+ ground state. The equation appropriate to this situation was derived by Gurvich and Korobov[15] and applied by them to O_2. It was subsequently applied to C_2 by Altman.[16] Since it has been used only very infrequently, however, a brief review of the derivation of the equation seems desirable.

In general, the partition function is the sum of Boltzmann factors for all quantum states, but in practice it is separated into factors for translation, rotation, vibration, etc. The translational factor is the same for any electronic state. But the rotational factor depends on R_e (or B_e) and the vibrational factor on ω_e. Hence these factors should be considered separately for each electronic state. Thus the complete partition function for a diatomic molecule becomes

$$q = q_{tr}(T,P) \sum_i q_{rot}(T,R_{e,i})\, q_{vibr}(T,\omega_{e,i})\, g_i\, e^{-\Delta\varepsilon_i/kT} \tag{7}$$

where $\Delta\varepsilon_i$ is the excitation energy above the ground state ($\Delta\varepsilon = T_e$), g_i is the electronic degeneracy, q_{rot} and q_{vibr} are the rotational and vibrational factors, and the sum covers all electronic states which make an appreciable contribution including the ground state for which $\Delta\varepsilon = 0$. The dependencies on P, T, R_e, ω_e are also indicated. The q's depend also on the mass of the atoms, and the symmetry. For polyatomic molecules the vibrational contribution becomes a product of several factors for the various modes of vibration.

Since the lowest electronic state will usually make the dominant contribution, it is convenient to rewrite equation (7) for a diatomic molecule as follows

$$q = q_o \sum_i \left(\frac{R_{e,i}}{R_{e,o}}\right)^2 \left(\frac{1-\exp(-hc\omega_{e,o}/kT)}{1-\exp(-hc\omega_{e,i}/kT)}\right)\left(\frac{g_i}{g_o}\right) e^{-\Delta\varepsilon_i/kT} \tag{8}$$

where q_o is the complete partition function for the ground state. Here the vibrational factor is approximated by that for a harmonic oscillator. Again the sum covers all states with an initial term of unity from the ground state. In this form it is easy to note the contributions of various states and the point at which the sum can be terminated without significant error.

For Sn_2 we choose the experimental value of 189 cm^{-1} for $\omega_{e,o}$ and the calculated values in Table VII for all of the other parameters. At 1600 K the sum in equation (8) is 2.93 which is only slightly less than the value 3 assumed before on the basis of a $^3\Sigma_g^-$ electronic state. A much greater change arises, however, from the reduction of $\omega_{e,o}$ from the value 300 cm^{-1} assumed before[10,11] to 189 cm^{-1}. The change in R_e is smaller but also significant.

The mass spectral data[10] were presented in the form of D_o^o values for a series of temperatures from 1472 to 1769 K calculated on the basis of a partition function with defined parameters. The correction to each D_o^o value is

$$\delta D_o^o = RT \ln(q''/q') \tag{9}$$

where q' was the originally assumed partition function and q" is the revised value now calculated. At 1600 K this ratio q"/q' is 1.43 which yields a δD_o^o of 1.15 kcal mol^{-1}. But these quantities vary significantly with temperature and the appropriate correction was applied to each of the original values of D_o^o. These D_o^o should not vary systematically with temperature of measurement. The original values were acceptable but showed a slight decrease, on the average, with increase in T. For the revised values this trend has reduced and is within the scatter arising from experimental sources. The revised D_o^o is 47.0 kcal mol^{-1} or 2.04 eV.

The mass spectrometric data can also be treated by the "second law" method whereby ΔH is calculated from the change with T of the fraction dissociated. When corrected to 0 K this yields D_o^o = 51 kcal mol^{-1}. This difference between D_o^o values of 4.0 kcal mol^{-1} is less than 5.2 kcal mol^{-1} reported previously. With the reasonably reliable partition function parameters now available, the "third law" value of 47.0 kcal mol^{-1} is to be preferred.

Ackerman, et al.,[10] discuss the uncertainty in their value from various sources. The uncertainties in the partition function are now largely removed. The remaining uncertainties are purely experimental and should not exceed about 2.5 kcal mol^{-1} or 0.1 eV.

Our calculated dissociation energy for Sn_2 is 1.86 eV which agrees quite well with this experimental value of 2.04 ± 0.1 eV when it is considered that in the calculation it was not feasible to allow for exactly the same amount of intra-atomic electron correlation in the molecule and the dissociated atoms.

V. Concluding Remarks

While these results have been discussed primarily in terms of spin-orbitals, they are fully consistent with the general picture given earlier[17] for relativistic molecular spinors based on $p_{1/2}$ and $p_{3/2}$ atomic spinors. Since the lower energy $p_{1/2}$ spinors are 1/3 $p\sigma$ and 2/3 $p\pi$, the diatomic molecular spinors based thereupon are either σ bonding and π antibonding if of g symmetry or σ antibonding and π bonding if of u symmetry. Schwartz, et al.,[18] have presented a calculation for Au_2^+ which illustrates and corroborates this concept. For Pb_2 the simplest relativistic configuration would occupy fully both the $(1/2)_g$ and the $(1/2)_u$ molecular spinors which would yield no bonding. In fact, of course, there is mixing with $p_{3/2}$ spinors which enhances the σ bonding of the $(1/2)_g$ spinor and the π bonding of the $(1/2)_u$ spinor. In the limit this shift would yield the Λ-S configuration $\sigma_g^2\pi_u^2$ which is the dominant configuration as shown in Figure 5. But the bond in Pb_2 is much weaker than would be expected on a nonrelativistic basis and this weakness is directly related to the large spin-orbit effect for Pb. Schwarz, et al.,[18] presented simplified calculations for Pb_2 which further illustrate this picture.

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Table I. Dissociation Limits of some Molecular States of Pb_2 and Sn_2 and Their Energies in cm^{-1}

Molecular States	Dissociated Atoms	Energies of Dissociated Atoms in cm^{-1}	
		Pb_2	Sn_2
0_g^+	$^3P_0 + {}^3P_0$	0.0	0.0
$0_g^-, 0_u^-, 1_g, 1_u$	$^3P_0 + {}^3P_1$	7819.4	1691.8
$0_g^+, 0_u^+, 1_g, 1_u, 2_g, 2_u$	$^3P_0 + {}^3P_2$	10650.5	3427.7
$0_g^+(2), 0_u^-, 1_g, 1_u, 2_g$	$^3P_1 + {}^3P_1$	15638.7	3383.6
$0_g^+, 0_u^+, 0_g^-(2), 0_u^-(2),$ $1_g(3), 1_u(3), 2_g(2),$ $2_u(2), 3_g, 3_u$	$^3P_1 + {}^3P_2$	18469.8	5119.5
$0_g^+(3), 0_u^-(2), 1_g(2), 1_u(2)$ $2_g(2), 2_u, 2_g, 3_u, 4_g$	$^3P_2 + {}^3P_2$	21300.9	6855.4
$0_g^+, 0_u^+, 1_g, 1_u, 2_g, 2_u$	$^3P_0 + {}^1D_2$	21457.9	10304.8

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^+
$\sigma_g^2\pi_u\pi_g$	$^3\Delta_u$, $^3\Sigma_u^+$, $^3\Sigma_u^-$, $^1\Delta_u$, $^1\Sigma_u^+$, $^1\Sigma_u^-$	$0_u^+(2)$, $0_u^-(2)$, $1_u(3)$, $2_u(2)$, 3_u
$\sigma_g\pi_u^2\pi_g$	$^5\Pi_g$, $^3\Phi_g$, $^3\Pi_g(4)$, $^1\Phi_g$, $^1\Pi_g(3)$	$0_g^+(5)$, $0_g^-(5)$, $1_g(9)$, $2_g(6)$, $3_g(3)$, 4_g
$\pi_u^3\pi_g$	$^3\Delta_u$, $^3\Sigma_u^+$, $^3\Sigma_u^-$, $^1\Delta_u$, $^1\Sigma_u^+$, $^1\Sigma_u^-$	$0_u^+(2)$, $0_u^-(2)$, $1_u(3)$, $2_u(2)$, 3_u

Table III. Numbers of Configurations

	RC[a]	Total
0_g^+	21	1185
1_g	23	1052
2_u	10	504
1_u	12	664
0_u^-	12	642
0_u^+	12	642

[a] RC meaning "reference configurations" is defined in the text.

Table IV. Orbital Exponents in Slater-Type Basis Functions (with Principal Quantum Numbers in Parentheses).

s	1.9021(4)	2.6828(5)
	0.8482(4)	1.6074(5)
p	1.5189(4)	2.3775(5)
	0.8599(4)	1.3523(5)
d	3.5804(4)	3.9532(4)
	1.6047(4)	1.5175(4)

Table V. Potential Energy Curves of Some Low Lying States of Pb_2

R	$0_g^+(I)$	$1_g(I)$	2_u	$1_u(I)$	2_g	0_u^-	$1_g(II)$	$0_g^+(II)$	0_u^+	$1_u(II)$	$^3\Sigma_g^-$	$^3\Pi_u$	$^1\Sigma_g^+$
3.5	.2970	-	-	-	-	-	-	-	-	-	-	-	.3009
4.0	.0662	.1286	.0661	.0692	.1721	.1020	.1641	.1060	.1093	-	.1641	.1019	.0705
4.7	.0367	.0558	.0361	.0413	.0833	-	.1113	-	.0726	.0811	.0922	.0653	.0795
5.0	.0119	.0306	.0310	.0353	.0612	.0602	.0785	.0765	.0657	.0732	.0704	.0598	.0832
5.3	.0029	.0216	.0316	.0356	.0503	.0594	.0673	.0694	.0650	.0730	.0597	.0595	.0814
5.5	.0006	.0193	.0342	.0378	.0519	.0610	.0632	-	.0668	.0749	.0570	.0616	.0794
5.7	.0006	.0197	.0382	.0405	.0465	.0640	.0613	.0636	.0701	.0772	.0573	.0656	.0799
6.0	.0025	.0235	.0449	.0475	.0482	.0689	.0617	.0625	.0757	.0825	.0604	.0724	.0805
7.0	.0175	.0436	.0714	.0688	.0709	-	.0719	.0687	-	-	.0857	.1005	.0979
9.0	.0318	-	-	-	-	-	-	-	-	-	.1176	-	.1186
11.0	.0322	-	-	-	-	-	-	-	-	-	-	-	-

Table VI. Potential Energy Curves for Several Low Lying States of Sn_2

R	$0_g^+(I)$	1_g	2_u	1_u	0_u^-	0_u^+	$1_u(II)$	2_g	$0_g^+(II)$	$1_g(II)$	$^3\Sigma_g^-$	$^3\Pi_u$	$^1\Sigma_g^+$
4.0	.0942	.1547	.1062	.1109	.1195	.1197	.1310	.1920	.1532	-	.1644	.1140	.1084
4.25	.0635	-	-	-	-	-	-	-	.0793	-	.0863	-	.0643
4.5	.0366	-	-	-	-	-	-	-	.0466	-	.0442	-	.0464
4.75	.0131	.0144	.0092	.0139	.0216	.0221	.0357	.0503	.0402	.0729	.0204	.0173	.0405
5.0	.0024	.0037	.0069	.0116	.0187	.0192	.0333	.0372	.0375	.0555	.0098	.0148	.0377
5.25	.0001	.0017	.0107	.0156	.0222	.0228	.0377	.0328	-	.0476	.0079	.0186	.0361
5.5	.0028	.0049	.0180	.0231	.0291	.0298	.0452	.0337	.0374	.0455	.0110	.0259	.0370
6.0	.0146	.0188	.0360	.0412	.0464	.0473	.0626	.0434	.0457	.0470	.0242	.0440	.0450
7.0	.0406	.0521	.0657	.0722	.0763	.0788	-	.0710	.0627	.0694	.0537	.0781	.0660
9.0	.0644	-	-	-	-	-	-	-	-	-	.0920	-	.0923
10.0	.0682	-	-	-	-	-	-	-	-	-	.0925	-	-

Table VII. Spectroscopic Constants of Several Low Lying States of Sn_2 and Pb_2 and the Corresponding Values Obtained Without the Spin Orbit Term

	T_e (cm^{-1})		R_e (Å)		ω_e (cm^{-1})	
State	Pb_2	Sn_2	Pb_2	Sn_2	Pb_2	Sn_2
0_g^+	0	0	2.97	2.76	103	197
1_g	4 150	342	2.94	2.75	124	205
2_u	6 670	1 477	2.70	2.62	119	218
1_u	7 570	2 509	2.71	2.62	119	220
2_g	10 130	7 159	3.03	2.81	105	178
0_u^-	12 920	4 084	2.75	2.63	106	219
1_g(II)	13 320	9 964	3.07	2.95	100	88
0_g^+(II)	13 640	8 002	3.18	2.78	74	116
0_u^+	14 130	4 192	2.74	2.63	115	221
1_u(II)	15 820	7 260	2.73	2.62	123	232
$^3\Sigma_g^-$	12 400	1 694	2.95	2.75	126	204
$^3\Pi_u$	12 905	3 218	2.73	2.62	113	219
$^1\Sigma_g^+$	17 295	7 901	2.95	2.81	150	140

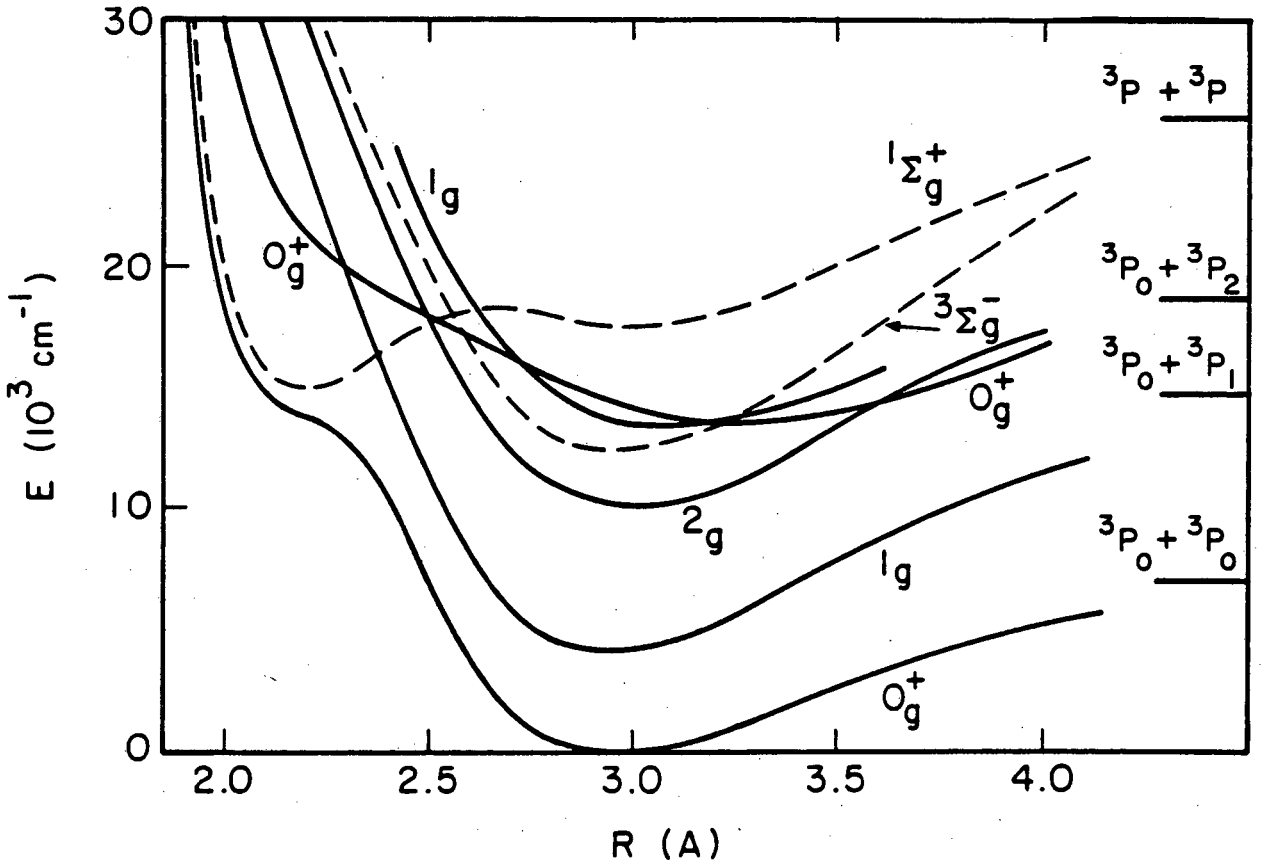

Figure 1. Calculated potential curves for g states of Pb_2. The dashed curves are computed without the spin-orbit term.

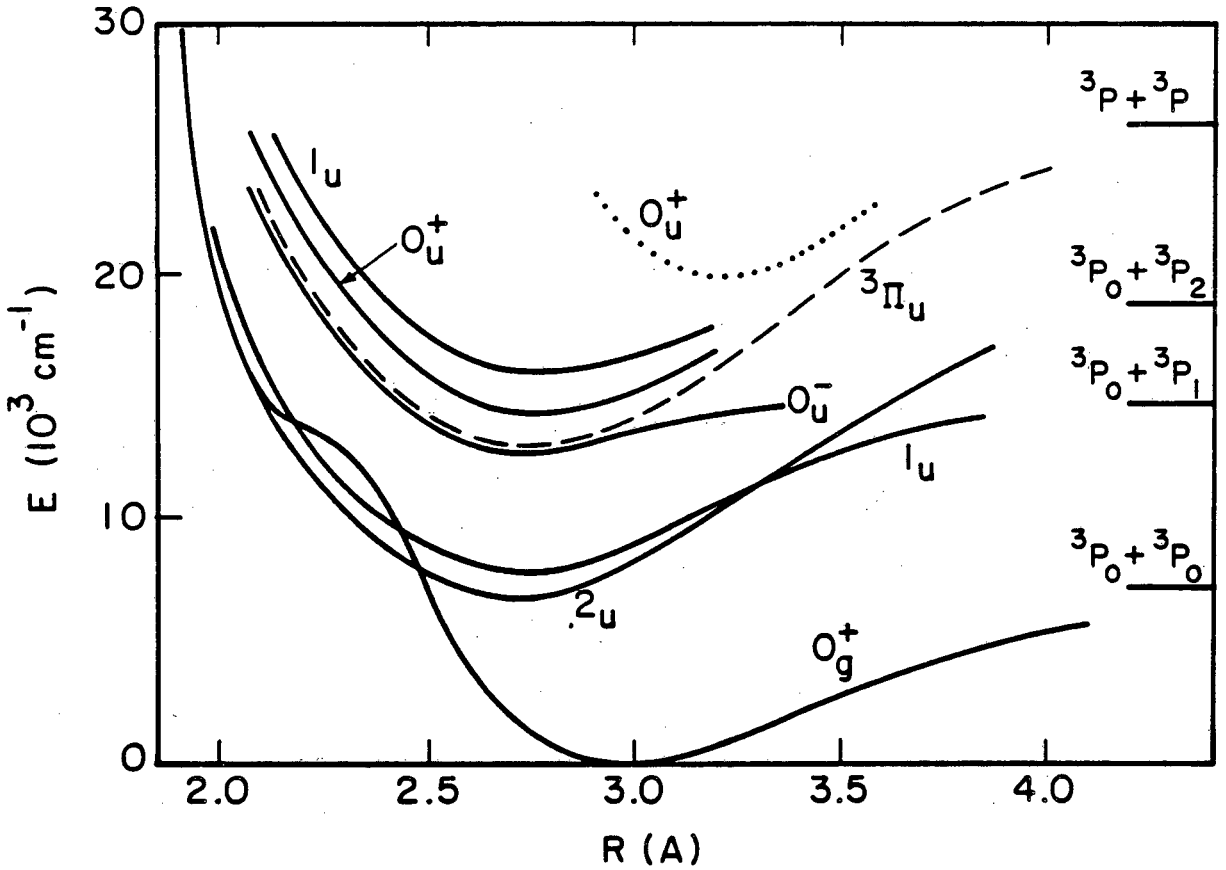

Figure 2. Calculated potential curves for u states and the ground 0_g^+ state of Pb_2. An estimated curve at the experimental T_e is also given for the upper 0_u^+ state.

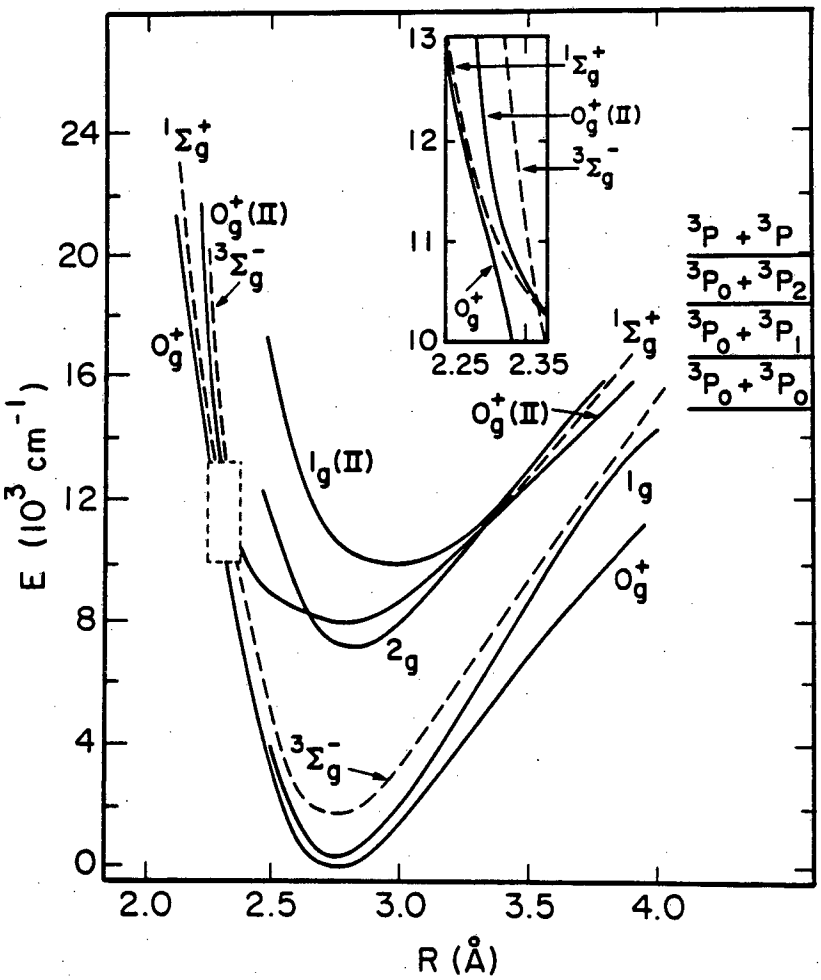

Figure 3. Calculated potential curves for the g states of Sn_2. An inset shows the details of the avoided crossing of the two 0_g^+ curves and the crossing of the related $^1\Sigma_g^+$ and $^3\Sigma_g^-$ curves without SO.

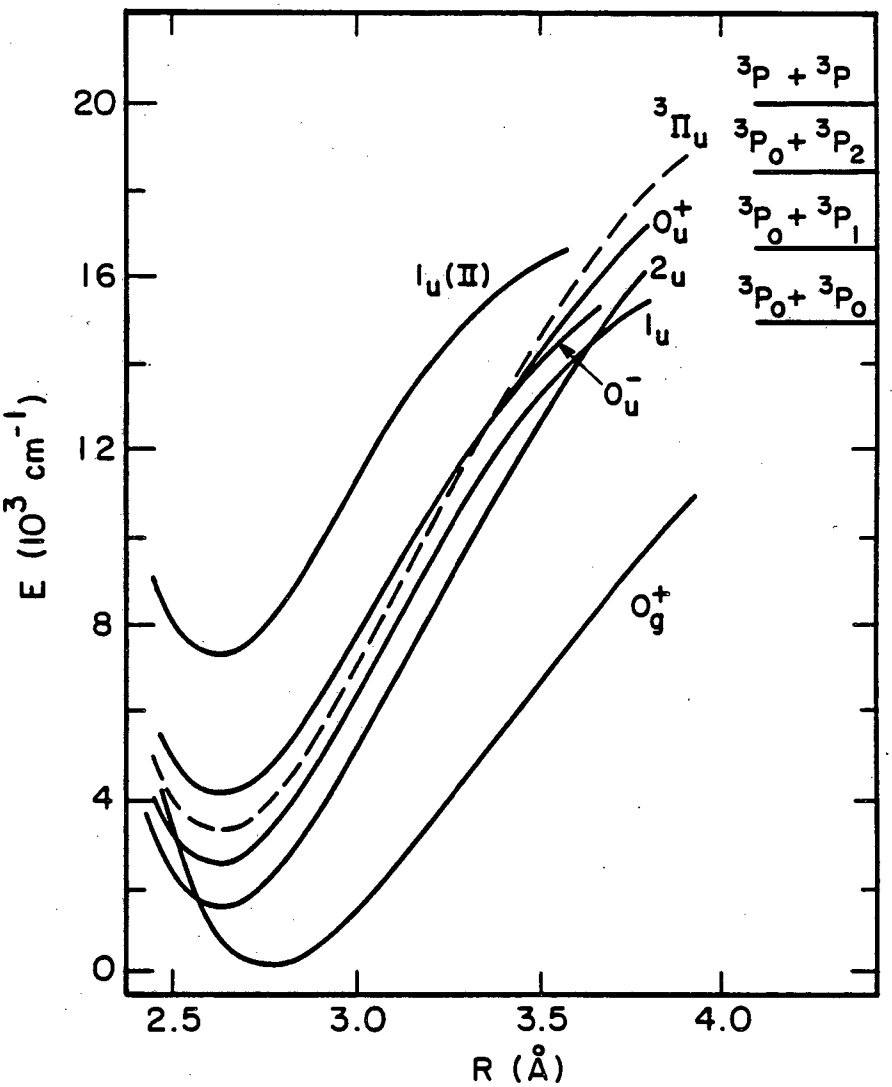

Figure 4. Calculated potential curves for the u states and the ground 0_g^+ state of Sn_2.

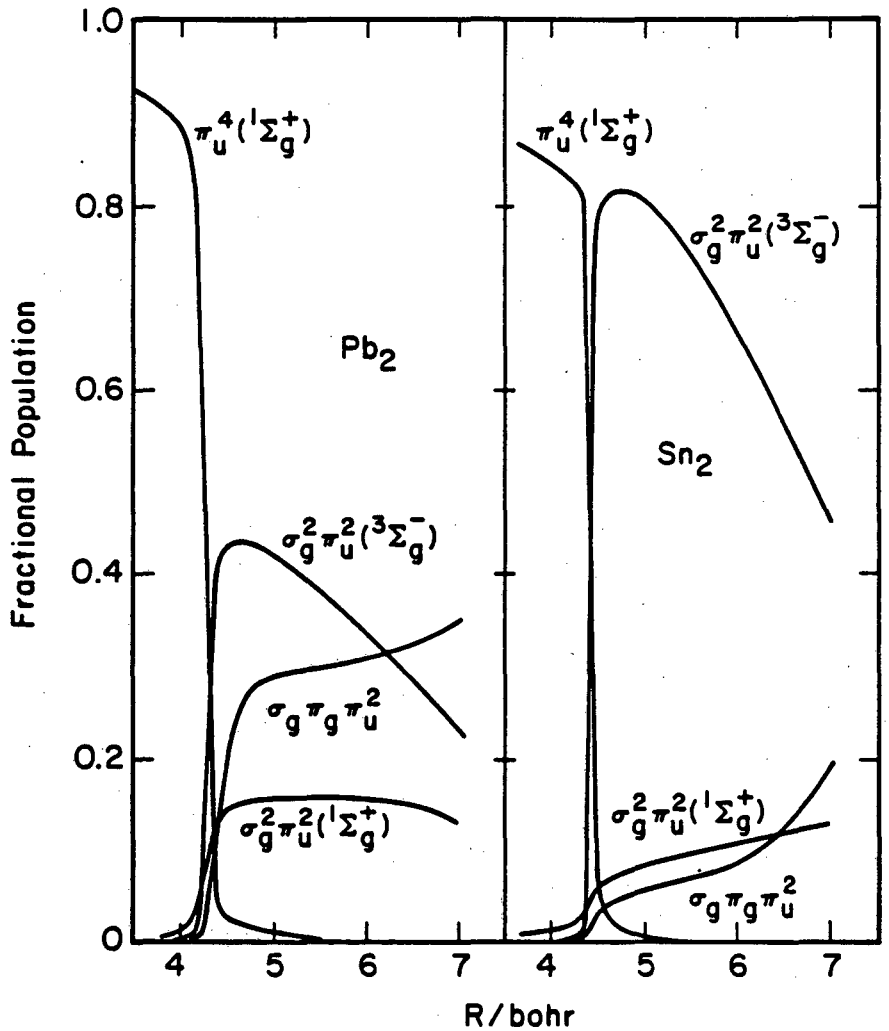

Figure 5. Fractional populations of various Λ-S configurations for Pb_2 and Sn_2.

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