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AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVISTIC EFFECTS. IV. POTENTIAL ENERGY CURVES FOR THE GROUND AND SEVERAL EXCITED STATES OF AU2

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AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVI[STIC] EFFECTS. IV. POTENTIAL ENERGY CURVES FOR THE GROU[ND] AND SEVERAL EXCITED STATES OF AU_2

Walter C. Ermler, Yoon S. Lee,
and Kenneth S. Pitzer

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Ab Initio Effective Core Potentials Including Relativistic Effects. IV. Potential Energy Curves for the Ground and Several Excited States of Au_2

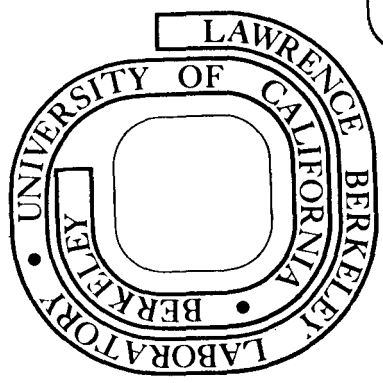Walter C. Ermler,[a] Yoon S. Lee, and Kenneth S. Pitzer

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Abstract

The ground and excited states of Au_2 are studied using ab initio averaged relativistic effective core potentials (AREP) and MCSCF-CI procedures. Spin-orbit effects are included in the excited states derived from $^2S_{1/2} + {}^2D_{3/2}$ and $^2S_{1/2} + {}^2D_{5/2}$ atomic states using an empirical procedure. The ground state dissociation energy is calculated to be 2.27 eV as compared to the experimental value of 2.31 eV. The calculated energies for the two spectroscopically allowed 0_g^+ to 0_u^+ transitions and other molecular parameters also agree reasonably with experiment.

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I. Introduction

There were several reasons for the choice of diatomic gold for an early study in relativistic molecular quantum mechanics. The dissociation energy is anomalously large, larger even than for Cu_2 whereas Ag_2 has a much smaller dissociation energy. Also Au_2 is isoelectronic with the mercurous ion Hg_2^{++} which is unique in its stability as a dimeric dipositive species. Also our present theoretical methods appeared to be adequate at this point for the treatment of a molecule where the primary bond was based on s orbitals as is explained below.

All-valence-electron calculations on the ground and several excited states of Au_2 are presented here as the fourth paper in a series dealing with the use of _ab initio_ effective core potentials (EP). Paper I[1] describes the formal procedure for deriving the EP's and reports results for the Xe and Au atoms, Paper II[2] presents SCF calculations on the ground, positive ion, and $6s\sigma_g$ Rydberg states of Xe_2, and Paper III[3] contains the first calculations using these methods on the ground state of Au_2 employing relativistic basis functions in which the results include the effects of spin-orbit coupling directly by the use of an EP defined in terms of two-component spinors. In addition comparisons with other forms of EP's, both relativistic and non-relativistic, are discussed in Paper III.

The Au_2 molecule was chosen as a test system because, as discussed in Paper I, it may be logically treated as a 22-valence electron system with the ground state predominantly being a 6s-6s σ_g bonding state and the low-lying excited states coming from the $5d^9 6s^2$ configuration leading to twelve states (in standard LS coupling notation) $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^3\Sigma_g^+$, $^3\Sigma_u^+$, $^1\Pi_g$, $^1\Pi_u$, $^3\Pi_g$, $^3\Pi_u$, $^1\Delta_g$, $^1\Delta_u$, $^3\Delta_g$, and $^3\Delta_u$. The $^2D_{5/2}$ and $^2D_{3/2}$ states of Au are 1.136 and 2.558 eV above the ground ^2S state whereas the next levels ($^2P_{1/2}$ and $^2P_{3/2}$) are at 4.632 and 5.105 eV.[4] Hence the treatment of the ^2D valence states should constitute a reasonably "clean" set in the sense of not being strongly perturbed by other low-lying states of the same symmetry. The availability of experimental results for the ground and some of the excited states allows us to make some comparisons with various spectroscopic constants.

Because the spin-orbit splitting of the $^2D_{5/2}$ and $^2D_{3/2}$ levels of Au is so great (1.522 eV), the description of excited electronic states of Au_2 in terms of $\omega-\omega$ coupling would appear to be most appropriate. The twelve LS symmetries above are combined using an empirical model[6] based on the atomic spin-orbit splitting to yield states of 0_g^+, 0_u^+, 0_g^-, 0_u^-, 1_g, 1_u, 2_g, 2_u, 3_g, and 3_u symmetry in Hund's coupling case c ($\omega-\omega$) notation. The observed molecular electronic states may then be compared directly with calculated results.

The following two sections describe the form of the wavefunctions used in this study and the methods of introducing

spin-orbit effects. The resulting potential energy curves are discussed in the last section. Some comments regarding analogous calculations on Ag_2 and Cu_2 are also included.

II. Calculations

The wavefunctions for the twelve LS-coupling symmetries arising from the interaction of $^2S + {}^2S$ and $^2S + {}^2D$ atomic states were computed using a model of the Au atom whereby the 68 core electrons were replaced by an averaged relativistic effective core potential (AREP), as described in Paper III, and the 11 valence electrons $(\ldots 5d^{10} 6s)$ were described by a valence basis set of two 2s, two 2p, two 3d, and one 4f Slater-type functions (STF). The AREP was represented as a numerical function including angular symmetries up to $\ell = 4$ (g-type) as the "residual potential" (see Paper III).

The (2s 2p 2d 1f) STF set (see Paper III) was determined by first fitting the s, p, and d-type pseudo-orbitals as two-term expansions then fully optimizing the exponents in atomic calculations for various LS-states in the field of the AREP. The 4f-type STF was optimized in ground-state SCF calculations on Au_2 near R_e and resulted in an energy lowering of about 0.003 a.u.

To insure that the molecular wavefunctions for the ground state of Au_2 was sufficiently flexible to allow for the proper dissociation to two ^2S Au atoms, it was necessary to include the two configurations allowed from the combination of the 6s electrons; $6s\sigma_g^2$ and $6s\sigma_u^2$. MCSCF calculations were carried

out incorporating these two configurations at 16 internuclear separations and are reported in Table I together with the analogous SCF (single-configuration) and CI (see below) results.

The molecular integrals for each of the 16 internuclear distances shown in Table I, including the matrix elements involving the AREP (see Paper III) were transformed over the MCSCF orbitals for the ground state and used in first-order[7] CI calculations designed as follows. The MCSCF orbitals were placed in three classes, the first corresponding to those derived from the 5d shell of Au, viz. $5d\sigma_g$, $5d\sigma_u$, $5d\pi_u$, $5d\pi_g$, $5d\delta_g$, and $5d\delta_u$. These orbitals were restricted to be fully occupied in the MCSCF calculations but their respective linear coefficients were optimized for each internuclear separation. The second class consists of the $6s\sigma_g$ and $6s\sigma_u$ orbitals that were optimized with respect to configuration mixing at each internuclear separation. The $6s\sigma_g$ orbital is dominant near R_e but the two configurations have equal coefficients as dissociation is approached. The third class is made up of the remaining orbitals that can be constructed from the basis set. This class is usually termed the "external" or "virtual" class of orbitals whereas the first two are termed the "valence" space. The inclusion of only the 5d and 6s/in the valence shells space may be rationalized on the grounds that the ^2P states of Au lie about 2 eV higher than ^2D states, as mentioned above.

To construct a list of configurations for the CI calculations, excitations are defined in terms of the distribution of the 22 valence electrons among the orbitals in the three

classes. Table II shows how the configurations were defined
for the twelve LS-symmetries desired and the number of con-
figurations for each electron distribution for $^1\Sigma_g^+$ symmetry.
The final electron distribution in Table II corresponds to the
double excitations of the two 6s electrons and would serve to
comprise a complete CI for the two electron (frozen 5d) system.
The importance of including these "bond doubles" as well as
the successive improvement of the ground state wavefunction of
Au_2 as more electron distributions are included is shown in
Fig. 1. The 6s valence (VCI) 6s first-order (FOCI) binding
energies $(E(R = 4.75)-E(R = 20.0) \cong D_e = 0.91$ eV) are the same
since only the two MCSCF configurations are allowed. The
additional 10 single excitations, which would allow for orbital
relaxation effects,[7] yield no contribution because the two
valence configurations were optimized in the MCSCF procedure.
The curve for the complete VCI (distributions 1, 3, and 4) is
slightly lower (0.1 eV) than the 6s VCI due to some effects
coming from inclusion of 5d(Class I) excitations into the 6s
orbitals (Class II). The addition of the 5d FOCI configurations
(distributions 5, 6, and 7) causes a significant increase in
binding energy due to the effects of relaxation and polarization
of the orbitals arising from the 5d shells of the Au atoms.
Finally it is seen in Fig. 1 that the "bond doubles" (distri-
bution 8) results in an additional increase in the binding
energy of about 0.3 eV to yield a D_e value of 2.27 eV. This
change shows the importance of including this class of configu-
rations, or conversely, the degree of reliability of the first-
order method (distributions 1-7) in describing the ground state

of Au_2. It should also be pointed out that the inclusion of configurations that correspond to excitations of one or more electrons from the 5d-shells with one electron residing in the external space result in the inclusion of 0.3 eV of atomic correlation energy (lower two curves of Fig. 1). This effect is due to atomic excitations and should be nearly constant for all internuclear distances. The upper two curves have dissociation limits that are precisely the sum of two ^2S atomic SCF energies.

III. Spin-Orbit Interaction

In order to obtain the states corresponding to Hund's coupling case c (ω-ω coupling), the calculated LS states from $^2S + ^2D$ atomic asymtote were corrected with an empirical model[6] based on the experimental atomic spin-orbit splittings $^2D_{3/2}$ and $^2D_{5/2}$. All the ω-ω coupled states from $^2S + ^2D_{3/2}$ and $^2S + ^2D_{5/2}$ atomic asymtotes can be obtained as roots to the spin-orbit matrices given in Appendix 1 with $\zeta = .6087$ eV. Since the contribution from the ion pair ($Au^+ + Au^-$) accounts for all the bonding of the first $^1\Sigma_u^+$ state, it was necessary to modify the spin-orbit matrix for 0_u^+ states that come from the mixing of $^3\Pi_u$ and $^1\Sigma_u^+$ states. Instead of solving the 2 x 2 matrix for 0_u^+ states, three LS states were included in the spin-orbit matrix as shown in Appendix II. This approximation is based upon two additional assumptions. First, the spin-orbit splitting of ion pair states is zero, which is rigorously true for atomic ions. Second, the two lower lying $^1\Sigma_u^+$ states are composed of ion pairs and ^2S and ^2D atoms,

which is a reasonable approximation as can be estimated from CI coefficients. Then the contributions from $^2S + {}^2D$ atoms can be calculated using CI coefficients as shown in Appendix II. This modification is not used for O_g^+ states since the ion-pair contributes little to the first excited $^1\Sigma_g^+$ state

In order to obtain the experimental energy separation for the atomic limits, the energies of all the excited states are shifted by .305 eV relative to the ground state.

IV. Results and Discussion

The calculated potential curves for the excited states that have allowed transition moments from the ground state are shown in Fig. 2. The circle in Fig. 2 indicates the site of an avoided crossing of 1_u states if a CI calculation were done in the ω-ω coupled configurations. All other u states are shown in Fig. 3. Potential curves of calculated g states appear in Fig. 4. Vertical transition energies of these states calculated at the internuclear distance of 4.5 a.u. are given in Table III. They can be of some interest for certain applications and are useful as an additional guide for identifying the curves in Figures 2, 3, and 4.

Spectroscopic constants were calculated for states that have D_e larger than 0.3 eV and summarized in Table IV with the experimental results.

The spectroscopic information on Au_2 is given by Ames and Barrow[5] and by Kleman, et al,[8] who also cite earlier work. The fact that gold has but a single isotope allowed resolution of rotational structure[5] and yielded the precise interatomic distances which are given in Table IV together with other spectroscopic parameters. The dissociation energy of the

ground state is obtained from mass spectrometric experiments, most recently by Kordis, et al.[9] Their result, D_o = 52.9 ± 0.5 kcal/mole agrees well with earlier work including the value 51.5 ± 2.2 kcal/mole from Ackerman, et al.[10] With correction for zero point energy one obtains D_e = 2.305 ± 0.02 eV.

The values of 1.00 eV for the A 0_u^+ state and 1.78 eV for the B 0_u^+ state are calculated from the experimental T_e values of corresponding states[5] using the dissociation energy of the ground state and the atomic excitation energies to $D_{5/2}$ and $D_{3/2}$ states, respectively. It may be noted that simple extrapolations of vibrational levels yield D_e values of 1.41 eV and 1.47 eV for the A 0_u^+ and B 0_u^+ states, respectively.

One might have expected to observe also transitions to the 1_u state at 2.64 eV but this feature is evidently less intense than the X-A bands at nearly the same energy. Since the large transition dipole arising from the molecular ion-pair state falls only into the 0_u^+ symmetry, the lower intensity for the transition to the 1_u state is not surprising.

The agreement of calculated and experimental dissociation energies for the ground state is fortuitously good; that for R_e and ω_e reasonable. Although there is as much as 0.1 Å difference in calculated and experimental R_e values, it is interesting to note that the calculations reproduce the correct order with A 0_u^+ longest and B 0_u^+ intermediate. The total energies of excitation to the A and B states are also fitted quite well. Indeed the entire pattern of agreement with experimental values is remarkable and probably somewhat

fortuitous. All important aspects of the lower energy states of Au_2 appear to be appropriately taken into account by the relativistic E.P. methods adopted.

It is also recognized that most states coming from the $^2S + {}^2D_{3/2}$ asymptote and some repulsive states from the $^2S + {}^2D_{5/2}$ could be changed through the configuration mixing in ω-ω coupling case since the energy of the $^2D_{5/2} + {}^2D_{5/2}$ atomic asymptote is lower than that of $^2S + {}^2D_{3/2}$. However, there are no 0_u^+ or 0_g^- states arising from $^2D_{5/2} + {}^2D_{5/2}$; hence the calculated curves for these symmetries are unaffected. This last point is important for the B 0_u^+ state.

Calculations were also initiated for Cu_2 and Ag_2 following the same general system. While the results for the ground states give qualitatively correct sequences of R_e values and D_e values, several difficulties arose which made the results unsatisfactory on a quantitative basis. The same problems became even more serious for excited states.

For copper the most serious difficulty is the failure of SCF atomic calculations to reproduce, even approximately, the relative energies of the ^2S and ^2D states. Similar difficulties are known to arise for nickel. We understand that very extensive CI calculations[11] are required to remedy this situation and such extensive atomic CI would be beyond the scope of our present pattern.

For silver the problem arises from the fact that the ^2P excited state is somewhat lower than the ^2D state for the atom. Thus excitations involving both d and p orbitals must be

included in an adequate treatment. Furthermore, the methods
used here for spin-orbit effects in Au_2 would be inadequate
for Ag_2. In view of the more extensive efforts required to
properly deal with Cu_2 and Ag_2, it seemed better to present
just the results for Au_2 at this time.

ACKNOWLEDGEMENT

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Appendix I.   Spin-Orbit Matrices for $d^9s^2 + d^{10}s$ Molecules

$\Omega = 3$: $[E(^3\Delta) + \zeta]$

$\Omega = 2$:
$$\begin{bmatrix} E(^3\Delta) & & \\ \zeta/\sqrt{2} & E(^3\Pi) + \zeta/2 & \\ \zeta & -\zeta/\sqrt{2} & E(^1\Delta) \end{bmatrix}$$

$\Omega = 1$:
$$\begin{bmatrix} E(^3\Delta) - \zeta & & & \\ \zeta/\sqrt{2} & E(^3\Pi) & & \\ 0 & \sqrt{3}\zeta/2 & E(^3\Sigma^+) & \\ \zeta/\sqrt{2} & \zeta/2 & -\sqrt{3}\zeta/2 & E(^1\Pi) \end{bmatrix}$$

$\Omega = 0^-$:
$$\begin{bmatrix} E(^3\Pi) - \zeta/2 & \\ \sqrt{6}\,\zeta/2 & E(^3\Sigma^+) \end{bmatrix}$$

$\Omega = 0^+$:
$$\begin{bmatrix} E(^3\Pi) - \zeta/2 & \\ \sqrt{6}\,\zeta/2 & E(^1\Sigma^+) \end{bmatrix}$$

Appendix II

In an attempt to account for ion pair character let

$$\beta^2 = (C_{II}^2 + C_{III}^2)/(C_I^2 + C_{II}^2 + C_{III}^2),$$

where the C's are mixing coefficients corresponding to the respective (dominant) configurations in the first $^1\Sigma_u^+$ wave function,

$$
\begin{aligned}
&\text{I}\quad (s\sigma_g)(s\sigma_u), \quad - \quad \text{ion pair configuration}\\
&\text{II}\quad (d\sigma_u)(s\sigma_g)(s\sigma_u)^2, \left.\begin{array}{l}\\ \end{array}\right\} \;^2S + {}^2D \text{ configurations}\\
&\text{III}\quad (d\sigma_g)(s\sigma_g)^2(s\sigma_u).
\end{aligned}
$$

The energies of the 0_u^+ states are roots of

$$
\begin{bmatrix}
E(^3\Pi_u) - \zeta/2 & & \\
\beta(\sqrt{6}/2)\zeta & E_1(^1\Sigma_u^+) & \\
(1-\beta)(\sqrt{6}/2)\zeta & 0 & E_2(^1\Sigma_u^+)
\end{bmatrix}
$$

Table I.   Ground State Au_2 Valence Energies (a.u.)

R	E(SCF)	E(MCSCF)	E(CI)
3.0	−70.272820	−70.291183	−70.387333
3.5	.618155	.632900	.719504
4.0	.738262	.751744	.825669
4.25	.759430	.773288	.841041
4.5	.767895	.782712	.844318
4.75	.769278	.785526	.841337
5.0	.766328	.784477	.835026
5.25	.760811	.781305	.827011
5.5	.754218	.777429	.818684
5.75	.746473	.773001	.809870
6.0	.739423	.769366	.802415
7.0	.712174	.758443	.779374
8.0	.690422	.753765	.768405
9.0	.673762	.751926	.764050
10.0	.661266	.751150	.762353
20.0	.621691	.750536	.761078

Table II. Electron Distributions for CI Calculations
for 22-Valence Electron Au_2

Electron Distribution	I	II	III	No. $^1\Sigma_g^+$	Description
1	20	2	0	2	6s Valence CI(VCI)
2	20	1	1	10	6s First-order (FO CI)
3	19	3	0	2	5d VCI
4	18	4	0	6	5d VCI
5	19	2	1	88	5d FOCI
6	18	3	1	296	5d FOCI
7	17	4	1	402	5d FOCI
8	20	0	2	56	6s "Bond Doubles"
Total				862	

Table III. Vertical transition energies[a] (in eF) of selected excited states of Au_2 calculated at R = 4.50 a.u.

States	Vertical transition energies (eV)	States	Vertical transition energies (eV)
0_g^+	0.0	0_u^+	2.6529
	3.4550		3.6157
	5.6131		6.0626
0_g^-	2.5616	0_u^-	2.4482
	5.5161		3.0125
1_g	2.5710		5.7679
	3.9543	1_u	2.4482
	5.2359		2.6602
	5.7027		3.6495
2_g	3.2056		5.0216
	3.9443		5.8219
	5.1911	2_u	2.4688
3_g	3.1508		3.6563
			5.0316
		3_u	3.6002

[a] The energy scale shown in the figures can be obtained by adding the energy of the ground 0_g^+ state (-2.265 eV).

Table IV. Au_2 Spectroscopic Constants

State		R_e(Å)	D_e(eV)	ω_e(cm^{-1})	T_e(eV)
X 0_g^+	Calc.	2.37	2.27	165	0
	Expt.[a]	2.47	2.31[b]	191	0
A 0_u^+	Calc.	2.51	.79	121	2.61
	Expt.[a]	2.57	1.00	142	2.44
B 0_u^+	Calc.	2.50	1.38	146	3.55
	Expt.[a]	2.51	1.78	180	3.18
1_u	Calc.	2.44	.76	138	2.64
2_u	Calc.	2.43	.94	143	2.57
0_g^-	Calc.	2.44	.85	140	2.66
1_g	Calc.	2.44	.84	140	2.67
2_g	Calc.	2.61	.35	110	3.16
3_g	Calc.	2.61	.41	112	3.10

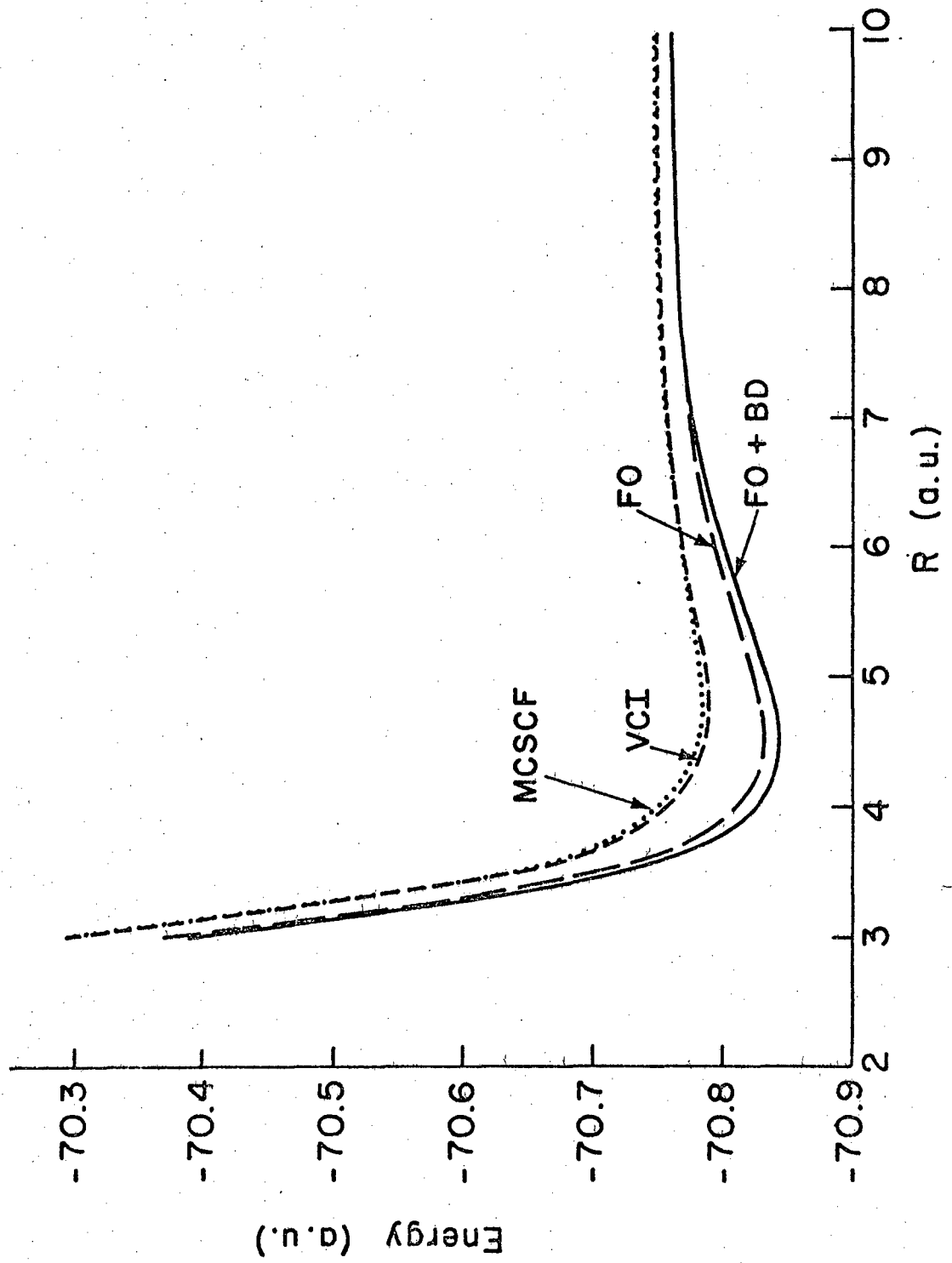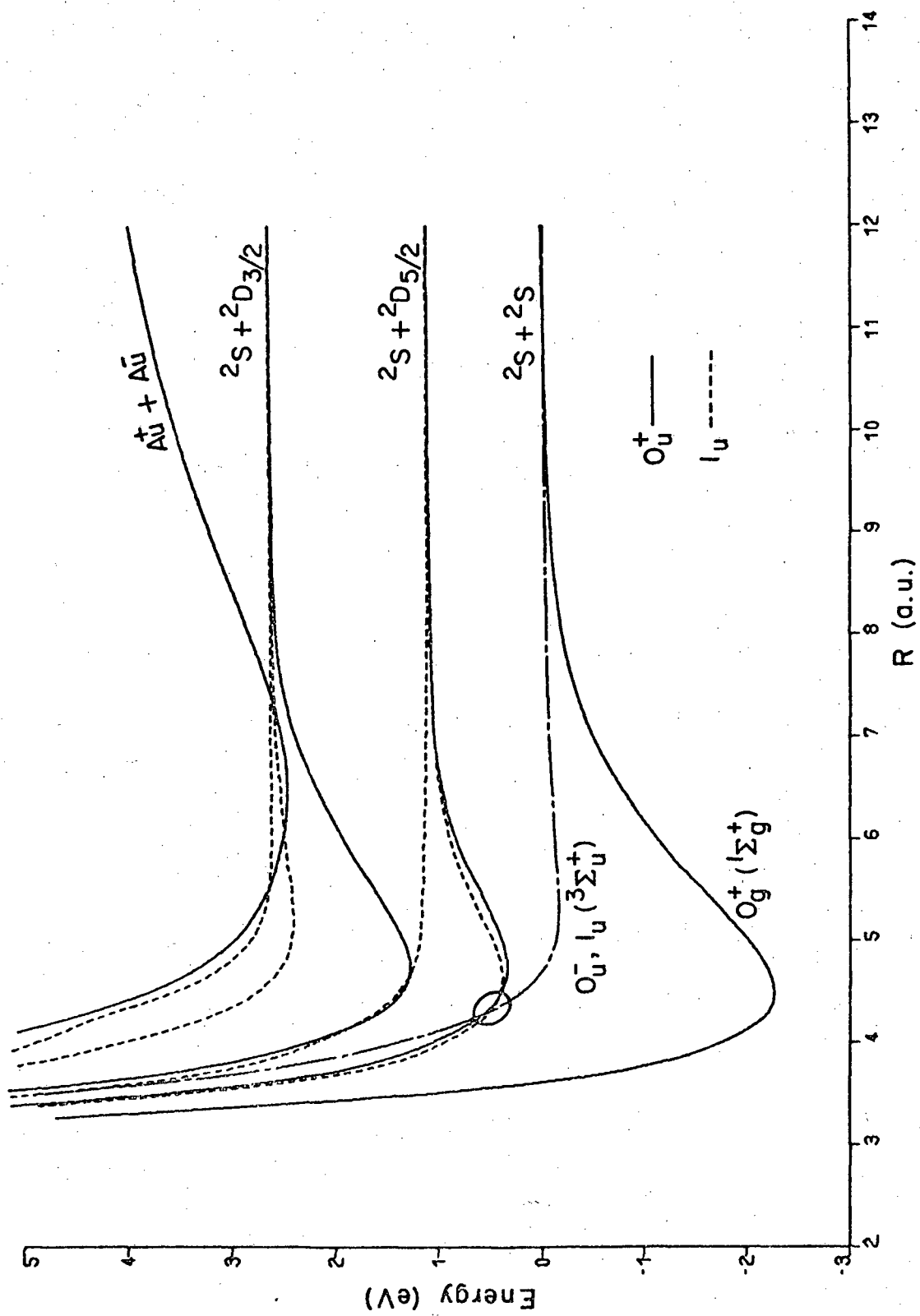[a] from Ref. 5.

[b] from Ref. 9.

Figure Captions

Fig. 1. Potential curves of 0_g^+ of Au_2 calculated with the various levels of configuration interactions (CI).
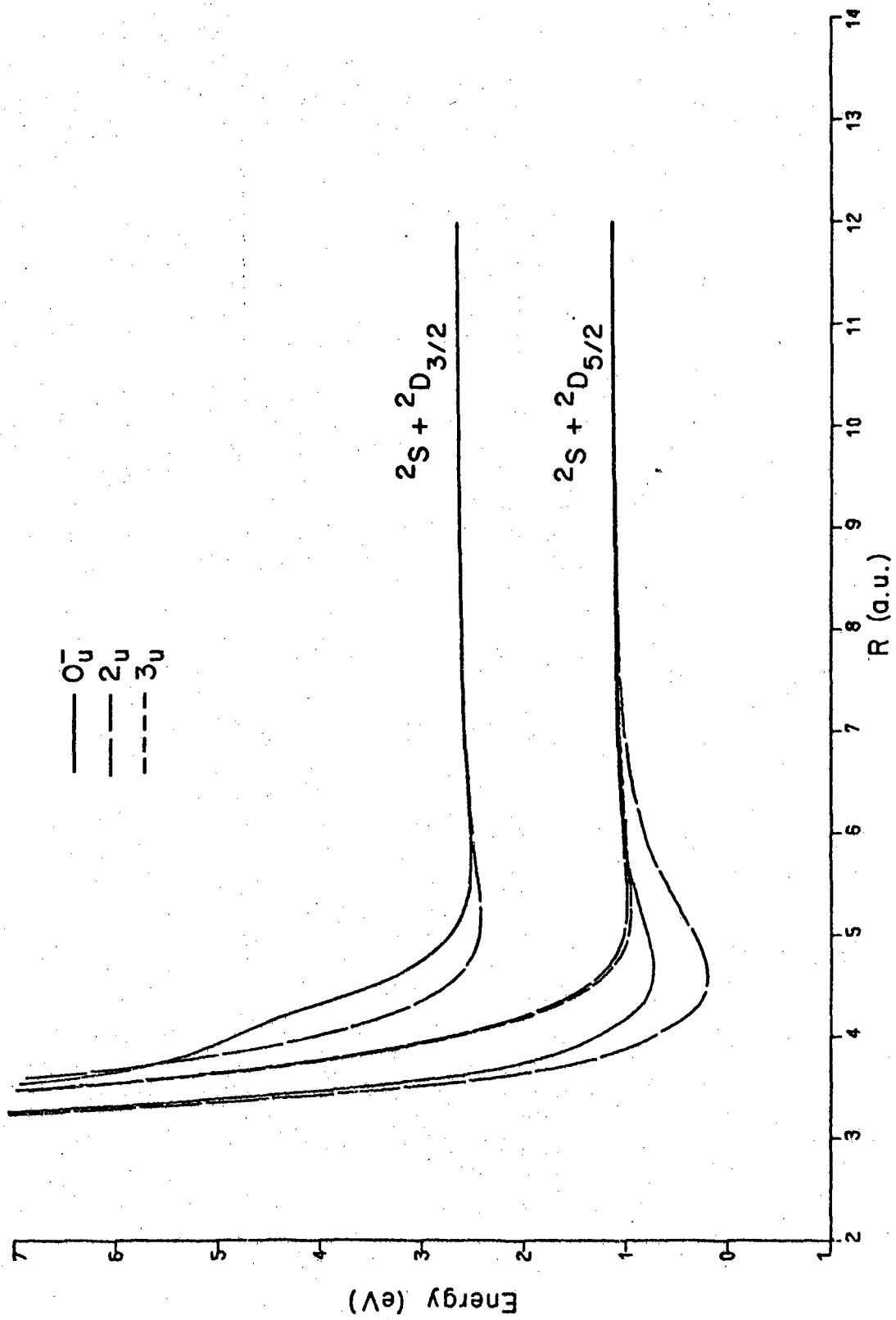
Fig. 2. Molecular states of Au_2 derived from the $^2S + {}^2S$ atomic asymtote and the spectroscopically allowed excited states from $^2S + {}^2D$ asymtote. Spin-orbit effects and ion-pair mixing are included in the calculation.
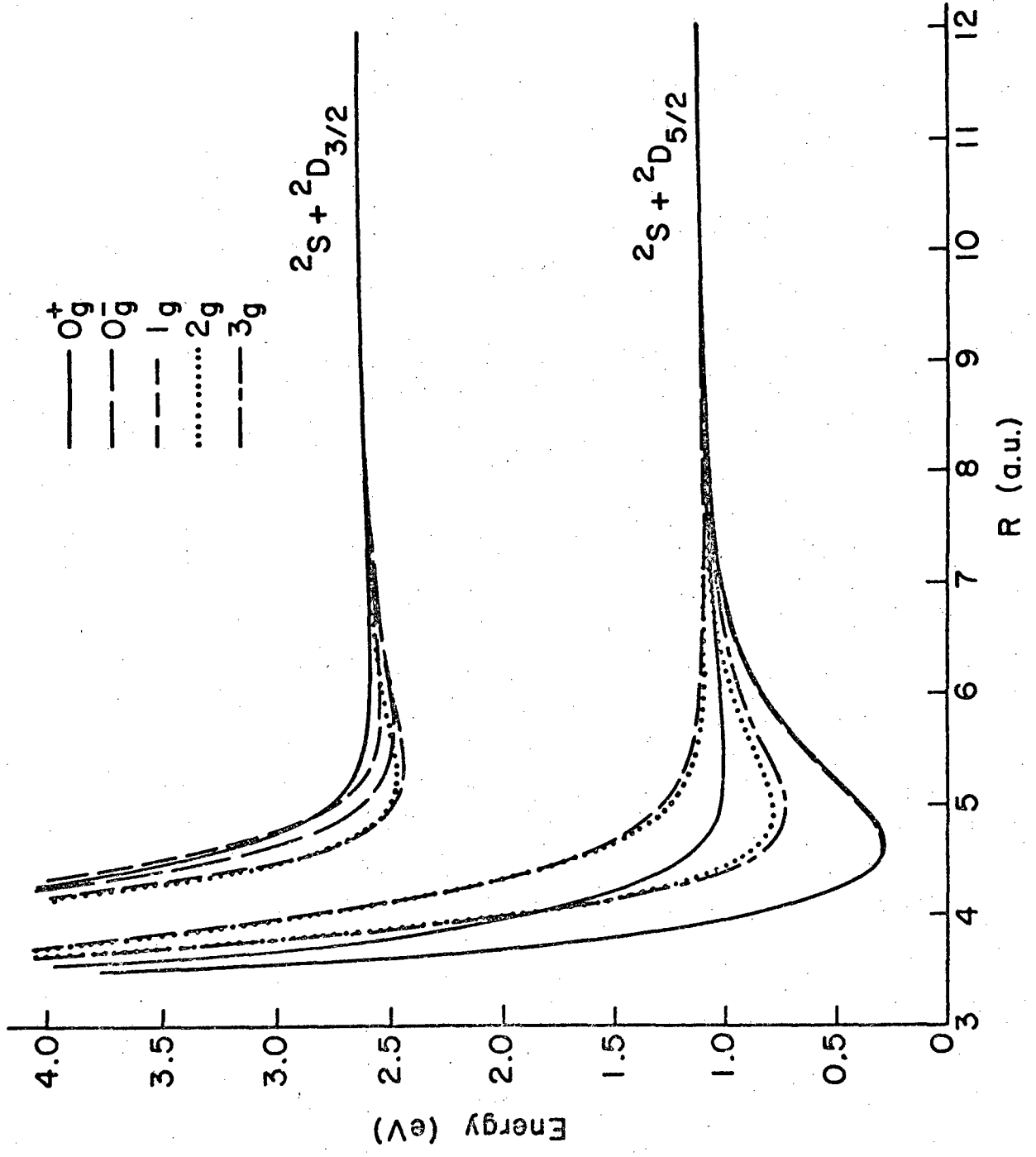
Fig. 3. 0_u^-, 2_u and 3_u states of Au_2 derived from $^2S + {}^2D$ atoms.

Fig. 4. 0_g^+, 0_g^-, 1_g, 2_g and 3_g states of Au_2 derived from $^2S + {}^2D$ atoms.

Energy (a.u.) vs R (a.u.) curves labeled MCSCF, VCI, FO, FO + BD.

$2_S + {}^2D_{3/2}$

$2_S + {}^2D_{5/2}$

0_u^-
2_u
3_u

R (a.u.)

Energy (eV)

Legend:
- 0_g^+
- 0_g^-
- 1_g
- 2_g
- 3_g

$^2S + {}^2D_{3/2}$

$^2S + {}^2D_{5/2}$

R (a.u.)

Energy (eV)

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