Theoretical Study of the Potential Energy Curves of the Series of Diatomic Radicals Me$_{II}$X

II. Application to BeCl and MgF Radicals

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The potential energy curves of some low lying electronic states of the diatomic radicals BeCl and MgF have been calculated. The calculation has been performed according to a stepwise procedure, outlined in a previous work. The potential energy curves are very similar to those of the mercury halide radicals, the electronic transitions of which can be employed for efficient laser apparatus.

Key Words: Electronic transition lasers – BeCl, potential energy curves of ~ – MgF, potential energy curves of ~.

1. Introduction

In a preceding paper [1] (hereafter referred to as I) we have outlined a scheme for calculating, by means of independent SCF procedures, the potential energy curves of some low lying electronic states of the Me$_{II}$X radicals, where Me$_{II}$ is a metal of groups IIA or IIB, and X is a halogen. The mercury halide radicals, HgCl, HgBr and HgI, which show electronic states which can be used for efficient visible and near U.V. lasers, belong to this series. Because of their electronic structure, all the members of the Me$_{II}$X series should have very similar potential energy curves; indeed, the curves we have calculated for the BeF radical show a close resemblance with those reported by Wadt, Hay and Dunning [2] for HgCl, HgBr and HgI. In this paper we present the potential energy curves for the two isoelectronic radicals BeCl and MgF. There are essentially two reasons for this calculation: the first is the lack of experimental curves to be used for a theoretical prediction of the transitions and their possible use; moreover these

radicals can be studied by an accurate ab initio calculation, while more approximate methods, such as some contraction of the basis set or an effective core potential, may be necessary for the other members of the series. The calculation scheme is the same we have employed in I, with a division of the procedure into successive steps which allows a more intuitive understanding as well as a greater reliability of the results.

2. Basis Functions

Our calculation programs utilize the Modified Gaussian Functions [3, 4]. For the choice of the orbital exponents (α), we consider the various electronic states originating from the dissociation of the molecules, with an energy within the limit of the dissociated states $Be^+ + Cl^-$ and $Mg^+ + F^-$. Since the energy of these two dissociated states can be evaluated respectively as 44 100 and 42 400cm^{-1} [5], the states to be taken into account are ^2P and ^1S (negative ion) of the halogens, ^1S, ^3P, ^1P and ^2S (positive ion) of the Me_{II} atoms. The state ^3S of Mg atom, lying under the ionic dissociation limit [6] has been omitted because it is too close to this limit.
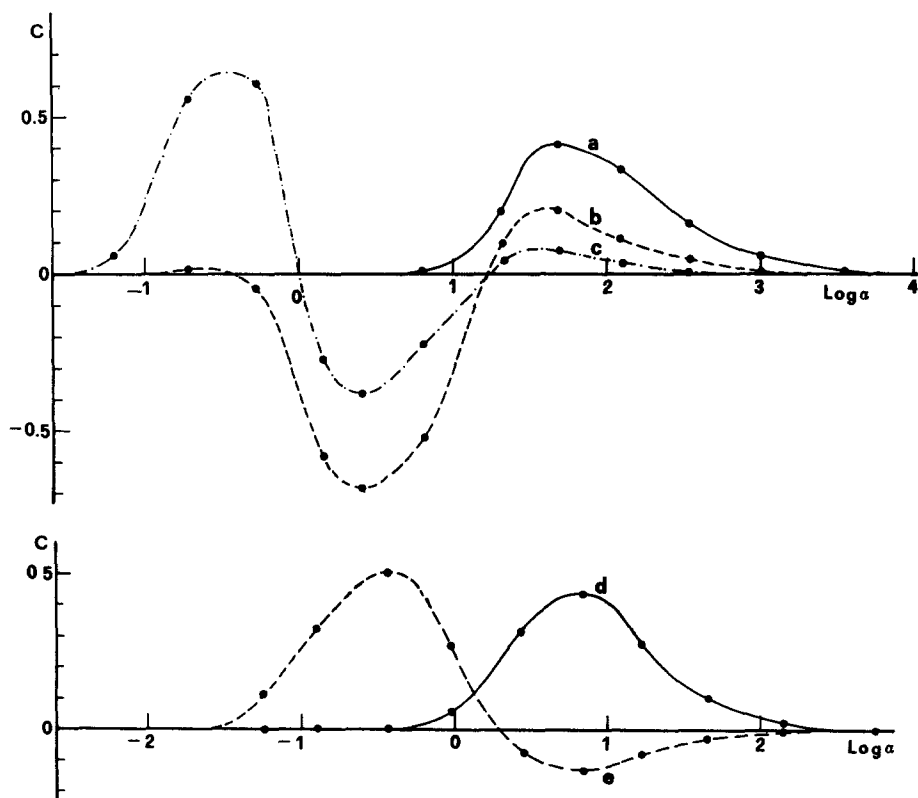

Fig. 1. Behaviour of the coefficients as a function of Log α (α = orbital exponent) for the Cl$^-$ ion. a: 1s; b: 2s; c: 3s; d: 2p; e: 3p
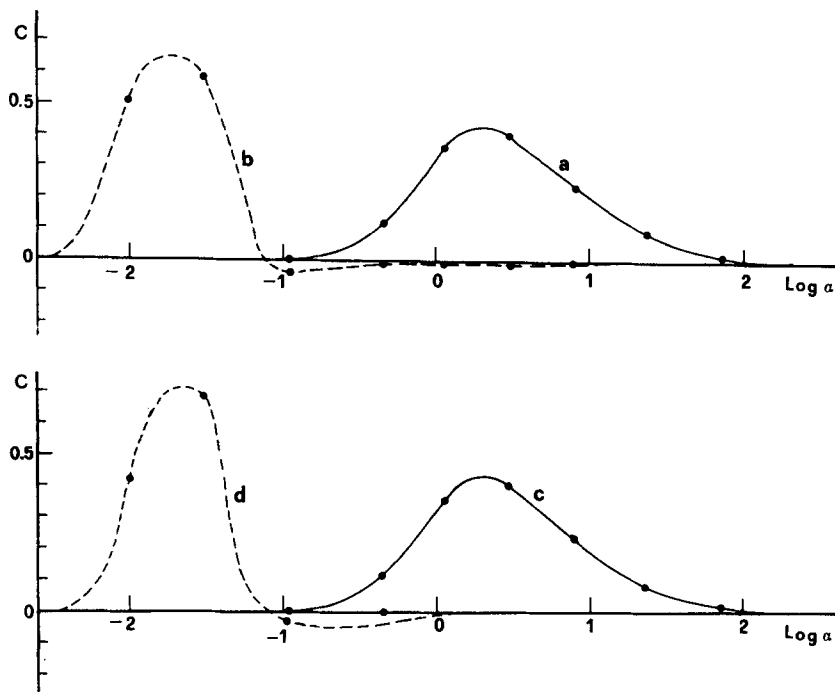
Fig. 2. As in Fig. 1. a: Mg* ^1P $2p$; b: Mg* ^1P $3p$; c: Mg* ^3P $2p$; d: Mg* ^3P $3p$

For the Be and F atoms the basis set is the same employed in I. In order to obtain a good representation of $3s$ and $3p$ orbitals of the Cl$^-$ ion we have added an s-type ($\alpha = 0.063$) and a p-type function ($\alpha = 0.056$) to the Huzinaga basis set [7]. The same basis set needs the addition of at least two expanded p-type functions ($\alpha = 0.03$ and $\alpha = 0.01$) for the description of the ^3P and ^1P states of the Mg atom. Figs. 1 and 2 show the curves of the coefficients of the basis functions versus Log α for the various states of Cl and Mg; we employ this method as a qualitative criterion to judge the goodness of the basis sets.

Table 1. Energy values (a.u.) of the BeCl radical in the various states (diabatic)

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$	$C\,^2\Sigma^+$	$D\,^2\Sigma^+$
3.0	−474.0914	—	—	—	—
4.0	−474.1403	—	—	—	—
4.5	−474.1176	—	—	—	—
5.0	−474.0912	−474.0253	−473.9366	−473.7821	−473.8578
6.0	−474.0479	−474.0405	−473.9822	−473.8271	−473.9053
8.0	−474.0476	−474.0472	−473.9631	−473.8549	−473.9603
9.0	−474.0477	—	−473.9508	−473.8612	−473.9733
10.0	−474.0477	—	−473.9401	−473.8663	−473.9802
15.0	−474.0477	—	−473.9066	−473.8672	−473.9811

Table 2. Energy values (a.u.) of the MgF radical in the various states (diabatic)

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$	$C\,^2\Sigma^+$	$D\,^2\Sigma^+$
2.0	−298.2302	—	—	—	—
2.5	−298.9449	—	—	—	—
3.0	−299.1118	−298.8916	—	—	—
3.3	−299.1305	—	−298.8702	—	—
3.5	−299.1295	—	—	—	—
4.0	−299.1082	−298.9849	−298.9186	—	—
5.0	−299.0147	−299.0066	−298.9772	—	—
7.0	−299.0185	—	−298.9632	−298.8944	−298.8595
8.0	−299.0190	—	−298.9469	−298.9021	−298.8633
10.0	−299.0192	—	−298.9211	−298.8837	−298.8663
15.0	−299.0192	—	−298.8868	−298.8733	−298.8601
17.7	−299.0192	—	−298.8765	−298.8779	−298.8653
20.0	−299.0192	—	—	−298.8773	−298.8656
21.5	−299.0192	—	−298.8664	−298.8799	−298.8667

3. Potential Energy Curves

We have taken into account, for both molecules, the diabatic states $X\,^2\Sigma^+$, $A\,^2\Pi$, $B\,^2\Sigma^+$, $C\,^2\Sigma^+$ and $D\,^2\Sigma^+$. The fillings are analogous to those of the corresponding states of BeF molecule in I. The orthogonality of the B, C and D states with the ground state was guaranteed by limiting the space of variability of one orbital, according to our SCF procedure for the excited states [8, 9]. The orthogonality
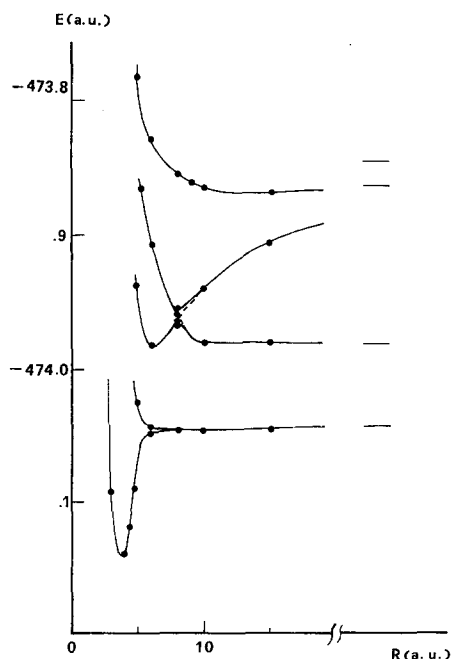

Fig. 3. Potential energy curves of BeCl radical. Dashed curve: diabatic; solid curve: adiabatic. On the right the dissociation limits are shown

constraint between the B, C and D states has not been imposed: the limitation introduced in our scheme would give an excessive restriction to the space of variability. On the other hand the calculated overlap between these states at various internuclear distances is always very small (less than 0.001), so that the
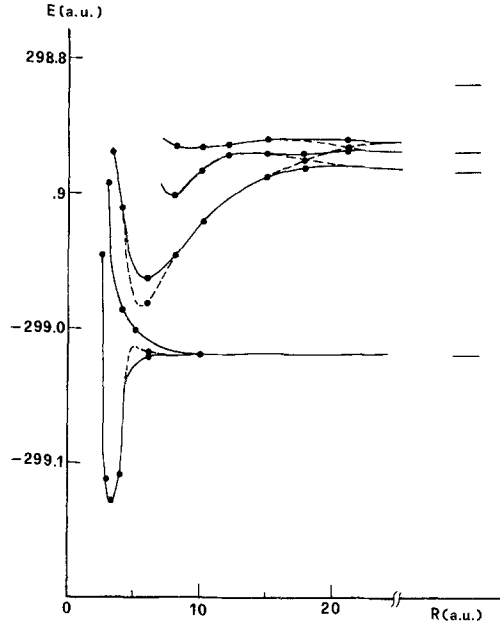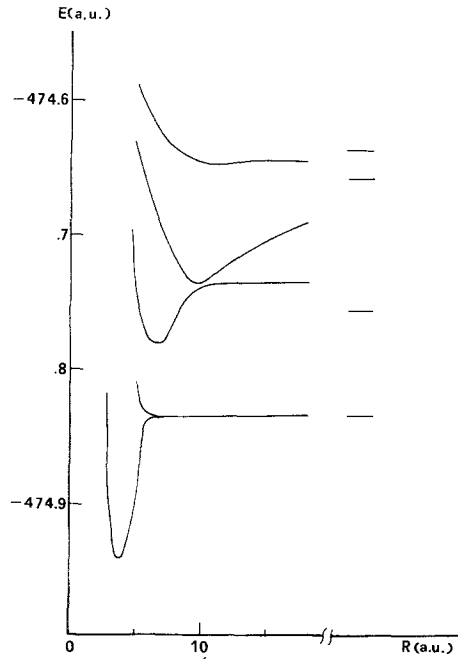

Fig. 4. As in Fig. 3, MgF radical

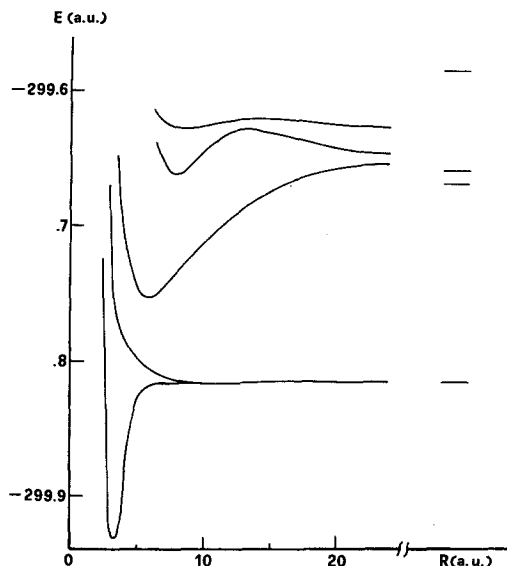**Fig. 5.** Adiabatic potential energy curves of BeCl radical, including the correlation energy

Fig. 6. As in Fig. 5, MgF radical

influence on the energy values is quite negligible. The energy values for the various diabatic states are reported in Tables 1 and 2.

The adiabatic potential curves have been obtained by means of a CI process between pairs of crossing states; the results are plotted in Figs. 3 and 4. The correlation energy has been calculated separately [10, 11] and has been added to the SCF-CI energy values. The total energy curves are reported in Figs. 5 and 6. It is to be pointed out that the correlation effects introduce remarkable modifications in the shape of the curve of the B state of the BeCl radical, while the curves of the other states are merely shifted toward lower energies.

References

1. Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **60**, 399 (1982)
2. Hay, P. J., Wadt, W. R., Dunning, T. H. Jr.: Ann. Rev. Phys. Chem. **30**, 311 (1979)
3. Golebiewsky, A., Mrozek, J.: Int. J. Quantum Chem. **7**, 623 (1973)
4. Golebiewsky, A., Mrozek, J.: Int. J. Quantum Chem. **7**, 1021 (1973)
5. Clementi, E., Roetti, C.: Atomic Data and Nuclear Data Tables, **14**, 177 (1974)
6. Atomic Energy Levels, Circular 467, U.S. Department of Commerce, National Bureau of Standards (1949)
7. Huzinaga, S.: Approximate Atomic Functions. Division of Theoretical Chemistry, Dept. of Chemistry, The University of Alberta, Canada (1971)
8. Colle, R., Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **48**, 251 (1978)
9. Colle, R., Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **48**, 257 (1978)
10. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **37**, 329 (1975)
11. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **53**, 55 (1979)