

Lawrence Berkeley National Laboratory

Recent Work

Title

RELATION BETWEEN ELECTRONIC STRUCTURE AND THE CHEMILUMINESCENCE ARISING FROM COLLISIONS BETWEEN ALKALINE EARTH ATOMS AND HALOGEN MOLECULES

Permalink

<https://escholarship.org/uc/item/5tf9g4vc>

Author

Schaefer lii., Henry F.

Publication Date

1972-06-01

RELATION BETWEEN ELECTRONIC STRUCTURE AND THE
CHEMILUMINESCENCE ARISING FROM COLLISIONS
BETWEEN ALKALINE EARTH ATOMS AND HALOGEN MOLECULES

David R. Yarkony, William J. Hunt,
and Henry F. Schaefer III

June 1972

AEC Contract No. W-7405-eng-48



For Reference
Not to be taken from this room

LBL-681

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

RELATION BETWEEN ELECTRONIC STRUCTURE AND THE CHEMILUMINESCENCE ARISING
FROM COLLISIONS BETWEEN ALKALINE EARTH ATOMS AND HALOGEN MOLECULES*David R. Yarkony, William J. Hunt[†], and Henry F. Schaefer III^{††}Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

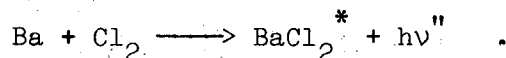
June 1972

ABSTRACT

The chemiluminescence ascribed by Jonah and Zare to radiative association of Ba and Cl₂ is examined in light of the electronic structure of the ground and excited states of alkaline earth dihalides. A simple discussion is first given in terms of the possible curve crossings and avoided crossings. In addition ab initio self-consistent-field calculations are reported for CaF₂ using an extended basis set. The ¹B₂ excited state, from which the molecule may radiate to the ground state, is predicted to have an equilibrium bond angle of 54° and bond distance of 4.06 bohrs. The vertical excitation energy to the ¹B₂ state is 7.3 eV and the vertical energy difference (¹A₁ - ¹B₂) at the ¹B₂ equilibrium geometry is 1.3 eV. These results appear consistent with the model proposed by Jonah and Zare. In addition, a variety of properties (dipole moments, field gradients, etc.) of CaF₂ are reported.

INTRODUCTION

The quest for a detailed understanding of the dynamics of molecular collisions has led to the development of several rather sophisticated experimental techniques.¹ Of these techniques one of the most promising is that of crossed-beam chemiluminescence, as developed by Ottinger and Zare.² As the name implies, the goal of this type of experiment is to observe product molecule emission spectra following a reaction carried out under well-defined single collision conditions. Perhaps the most interesting results obtained to date with this technique involved collisions between Ba and Cl₂. Based on their experimental findings, Jonah and Zare³ concluded that "the major source of chemiluminescent light is the two-body radiative association process



The reason for particular interest in this process is that bimolecular association reactions are normally considered highly improbable unless a third body is available to carry away the excess energy. If the interpretation of Jonah and Zare is correct, then the excess energy in the Ba + Cl₂ association is "carried away" by a photon.

The purpose of the present paper is to examine the work of Jonah and Zare in terms of the electronic structure the ground and excited states of the alkaline earth dihalides. Potential surfaces for the states of interest are first discussed from a simple empirical viewpoint. These simple ideas are then examined in light of a series of ab initio calculations on CaF₂. CaF₂ was considered the simplest molecule likely to be representative of BaCl₂, since it is usually assumed that dihalides involving the lighter atoms Be and Mg have

somewhat different properties. For example, electric deflection experiments⁴ indicate that BeF_2 and MgF_2 are linear, while CaF_2 , SrF_2 , and BaF_2 are bent. Hayes⁵ has argued that such differences are due to the fact that the unoccupied d orbitals (e.g. 3d in Ca) can participate in the bonding of the Ca, Sr, and Ba compounds, while such orbitals are not accessible in Be and Mg. Finally, having the CaF_2 wave functions at our disposal, several other properties of CaF_2 (not directly related to the chemiluminescence experiments) were computed.

QUALITATIVE DISCUSSION OF THE PROBLEM

The mechanism given by Jonah and Zare for the formation of BaCl_2 is as follows: a) Ba and Cl_2 approach in their electronic ground states b) an "electron jump"¹ occurs to a Ba^+Cl_2^- like potential surface, and c) an electronic transition occurs to the ground electronic state of BaCl_2 .

Accepting this line of reason, we have empirically constructed rough potential curves for the approach of Ba to Cl_2 . The data which go into this picture, Fig. 1, are the first and second ionization potentials of Ba (5.21 and 10.00 eV⁶), the dissociation energy of BaCl_2 (9.4 eV⁷), the dissociation energy of Cl_2 (2.48 eV⁸), and the electron affinities of Cl (3.61 eV⁹) and Cl_2 (2.38 eV¹⁰). In addition we estimated the excitation energy T_e of the $^1\text{B}_2$ state to be ~ 6 eV.

Some discussion of the symmetries of the electronic states of BaCl_2 is necessary. It is clear that the only one electronic state may be formed by bringing together ground state $\text{Ba}(^1\text{S})$ and ground state $\text{Cl}_2(^1\Sigma_g^+)$. This state must be totally symmetric. The same argument holds for $\text{Ba}^{++}(^1\text{S}) + \text{Cl}_2(^1\Sigma_g^+)$. In going from $\text{Ba}(^1\text{S}) + \text{Cl}_2(^1\Sigma_g^+)$ to $\text{Ba}^+(^2\text{S}) + \text{Cl}_2(^2\Sigma_u^+)$ we transfer (in a

Hartree-Fock or molecular orbital picture) an electron from a barium 6s orbital to a chlorine molecule $5\sigma_u$ orbital. The 6s orbital is of course totally symmetric, but the $5\sigma_u$ orbital becomes a b_2 orbital for C_{2v} symmetry. Thus, for the perpendicular approach of Ba to Cl_2 , the electron jump leaves the molecule in a state of 1B_2 symmetry.

Assuming (as do Jonah and Zare) the equilibrium geometry of the $Ba^+Cl_2^-$ like state to be C_{2v} , there will be one other important symmetry of approach, C_s . The occupied valence molecular orbitals for these two symmetries will be

C_{2v}	{	Ba Cl_2	$1a_1^2$	$2a_1^2$	$1b_1^2$	$1b_2^2$	$1a_2^2$	$3a_1^2$	$1A_1$	
		$Ba^+ Cl_2^-$	$1a_1^2$	$2a_1^2$	$1b_1^2$	$1b_2^2$	$1a_2^2$	$2b_2$	$3a_1$	${}^3B_2, {}^1B_2$
		$Ba^{++} Cl_2^-$	$1a_1^2$	$2a_1^2$	$1b_1^2$	$1b_2^2$	$1a_2^2$	$2b_2^2$		$1A_1$
C_s	{	Ba Cl_2	$1a'^2$	$2a'^2$	$1a''^2$	$3a'^2$	$2a''^2$	$5a'^2$	$1A'$	
		$Ba^+ Cl_2^-$	$1a'^2$	$2a'^2$	$1a''^2$	$3a'^2$	$2a''^2$	$4a'5a'$	${}^3A', 1A'$	
		$Ba^{++} Cl_2^-$	$1a'^2$	$2a'^2$	$1a''^2$	$3a'^2$	$2a''^2$	$4a'^2$	$1A'$	

It may also be useful to give the appropriate electron configurations for the linear symmetric molecule:

$D_{\infty h}$	{	Ba Cl_2	$1\sigma_g^2$	$1\pi_u^4$	$1\pi_g^4$	$2\sigma_g^2$	$1\Sigma_g^+$	
		$Ba^+ Cl_2^-$	$1\sigma_g^2$	$1\pi_u^4$	$1\pi_g^4$	$1\sigma_u$	$2\sigma_g$	${}^3\Sigma_u^+, 1\Sigma_u^+$
		$Ba^{++} Cl_2^-$	$1\sigma_g^2$	$1\pi_u^4$	$1\pi_g^4$	$1\sigma_u^2$		$1\Sigma_g^+$

We are now in a position to discuss in a rough and ready manner the dynamics of $Ba + Cl_2$ collisions. Coming in on the ground state Ba plus ground state Cl_2 potential curve, there is first a curve crossing with the $Ba^+ Cl_2^-$ surface. Actually the curves only cross if the Ba makes its approach along a perpendicular bisector of the Cl_2 molecule. Otherwise there is an avoided crossing between the two states, which for general (C_s) geometry are both of $^1A'$ symmetry. In a semi-classical picture there will be some probability P_1 of the molecule switching from the covalent $BaCl_2$ surface to the ionic $Ba^+ Cl_2^-$ surface at the avoided crossing separation.

Having undergone an electron jump to the $Ba^+ Cl_2^-$ surface, the Ba^+ and Cl_2^- will approach each other uneventfully until the $Ba^+ Cl_2^-$ surface is crossed by the $Ba^{++} Cl_2^=$ potential surface. Again the crossing will be avoided for all approaches except that of C_{2v} symmetry. At the avoided crossing there will be a probability P_2 of switching to the $Ba^{++} Cl_2^=$ surface; i.e. a second electron jump may occur. This second electron jump would place the molecule on the ground state potential surface, without the emission of a photon. At this point the $BaCl_2$ would of course have a great deal of excess energy and stable $BaCl_2$ would appear only if a third body were to carry away this excess energy. An alternate route for the disposal of this energy would be the formation of $BaCl + Cl$.

The radiative association process of Jonah and Zare can only (in the simplest picture) occur if the molecule does not switch from the $Ba^+ Cl_2^-$ to the $Ba^{++} Cl_2^=$ surface at the point of the above-discussed second crossing. The probability of this favorable path being followed is $P_1(1 - P_2)$. If $BaCl_2$ passes through this second avoided crossing, it finds itself in the bound (with

respect to $Ba + Cl_2$) $Ba^+Cl_2^-$ -like excited state, from which the desired ${}^1B_2 - {}^1A_1$ transition may occur. Therefore one of the purposes of the ab initio calculations to be reported here is to predict the properties of this 1B_2 electronic state of the alkaline earth dihalides.

It is important to recognize that for the other alkaline earth dihalides, the potential curves will be somewhat different from the $BaCl_2$ curves shown in Fig. 1. The energy levels for an alkaline earth atom A infinitely separated from a halogen molecule X_2 are

$$E(A^{++} + X_2^-) = IP(A) + IP(A^+) + D_0(X_2) + R(X^- - X^-) - 2EA(X)$$

$$E(A^+ + X_2^-) = IP(A) - EA(X_2)$$

$$E(A + X_2) = 0.0 \quad .$$

The quantity $R(X^- - X^-)$ is just the coulomb repulsion between two X^- ions separated by the neutral X_2 equilibrium bond distance. For sufficiently large $A - X_2$ separations, the potential curve for the $A + X_2$ interaction will be flat and the curves for the $A^+ + X_2^-$ and $A^{++} + X_2^-$ states will be given simply by the Coulomb attraction. We will assume that the covalent curve remains flat ($V = 0$) until after it is crossed by both of the ionic curves. The two crossing points will then be

$$R^{++} = 4/E(A^{++} + X_2^-)$$

$$R^+ = 1/E(A^+ + X_2^-) \quad .$$

It must be noted that this model assumes the bond distances of X_2 and X_2^- to be the same.

For BaCl_2 , R^+ is 9.61 bohrs and R^{++} is 6.15 bohrs. Thus the two crossings are well separated. The crossing between the Ba^+Cl_2^- and $\text{Ba}^{++}\text{Cl}_2^-$ curves is not given by the simple conditions outlined above but would appear to occur at a Ba - Cl_2 separation of ~ 5.5 bohrs. Of all the AX_2 molecules from BeF_2 to BaI_2 , the separation between the two crossings is greatest for BaF_2 , where $R^+ = 12.77$ bohrs and $R^{++} = 5.40$ bohrs. The distance between curve crossings is least for BeI_2 where $R^+ = 4.04$ bohrs and $R^{++} = 3.84$ bohrs. In fact this separation is so small that for BeI_2 it is doubtful that a model involving two distinct crossings is appropriate. The three electronic configurations probably simultaneously interact in a more complicated way for BeI_2 . In general, the curve crossings occur for much shorter A- X_2 distances as we go from the Ba to the Be containing dihalides. This behavior is due to the higher ionization potentials of the lighter atoms. Also, the separation between the two crossing points R^+ and R^{++} decreases in going from the difluorides to the diiodides. This is primarily due to the shorter bond distances for the lighter halogen molecules and the resulting larger values of the $\text{X}^- - \text{X}^-$ coulomb repulsion.

It should be clear that alkaline earth atom plus halogen molecule collisions provide an abundance of dynamic paths and outcomes. The above discussion is of course oversimplified and is intended only to illuminate some of the more important possibilities.

DETAILS OF THE QUANTUM MECHANICAL CALCULATIONS

For the reasons mentioned in the introduction, it was decided to carry out ab initio calculations on CaF_2 .

For Ca, Wachters¹¹ primitive gaussian basis of 14s and 9p functions was chosen. For the 1S ground state of the Ca atom, this basis yields a self-consistent-field energy of -676.7486 hartrees, as opposed to the near-Hartree-Fock energy of Clementi,¹² -676.7580 hartrees. For the present calculations, we contracted¹³ the (14s 9p) basis to (9s 5p) in the manner reported in our earlier work¹⁴ on ZnF_2 . The Ca atom SCF energy obtained with this basis was -676.7389 hartrees. Thus the primitive gaussian basis has an energy error of ≥ 0.0094 hartrees, while an additional 0.0097 hartrees is lost upon contraction. For each F atom Dunning's (9s 5p/4s 2p) basis¹⁵ was used. This "double zeta" basis¹³ is comparable in accuracy to that chosen for Ca.

Since the (4s 3d) 3D state of the Ca atom lies only 2.52 eV above the ground state, it can reasonably be argued^{5,16} that Ca 3d functions should be included in a basis set for molecules including the Ca atom. From Clementi and Raimondi's minimum basis set Slater function results¹⁷ for $V(\zeta_{3d} = 2.71)$ and $Ti(\zeta_{3d} = 2.37)$, it was decided that a 3d Slater function with orbital exponent $\zeta_{3d} = 2.0$ would be appropriate for Ca. Therefore a two gaussian fit, yielding $\alpha = 1.3088$ and 0.3877 , was made to this Slater 3d function. Then these two gaussian functions were used uncontracted in the CaF_2 calculations.

A somewhat surprising result of our calculations with this basis was the prediction of the 1A_1 ground state of CaF_2 to be linear. This is in disagreement with the electric deflection experiments of Klemperer and coworkers,⁴ who find CaF_2 to have a measurable dipole moment. Further, Calder *et al.*¹⁸ find CaF_2 to have a bond angle of $141 \pm 5^\circ$ in a matrix of solid krypton. Although we expect the bond angle of CaF_2 in the gas phase to be greater than 141° , it seems clear that this bond angle is less than 180° . Our results were

particularly surprising in light of the ab initio SCF prediction of Gole, Siu, and Hayes¹⁶ of a 145° bond angle for CaF_2 . Gole, Siu, and Hayes used a significantly smaller basis set than that described above. However the single contracted gaussian 3d function of Gole was more diffuse than either of our two 3d functions. Therefore we added a third primitive gaussian function, with exponent $\alpha = 0.1148$, to our basis. Although this third set of d functions lowered the total SCF energy by 0.0127 hartrees at $R(\text{Ca} - \text{F}) = 3.86144$ bohrs, $\theta = 180^\circ$, again CaF_2 was predicted to be linear.

The above ground state geometry predictions were somewhat disconcerting in light of the generally accepted belief¹³ that Hartree-Fock energies yield reliable bond angles. However, assuming CaF_2 really is bent, we feel that the present basis set, large as it is, is still inadequate for a reliable prediction of the CaF_2 bond angle. The fact that the CaF_2 bending force constant is very small is well known. In calculations on C_3 , another triatomic molecule with an unusually small bending frequency, it was recently found¹⁹ that a 4s 3p 1d basis on each carbon atom was required for reliable predictions. In this light, it seems probable that good agreement with experiment would be found for the CaF_2 bond angle if the F atom basis were enlarged. Since the ground state geometry of CaF_2 was not of prime importance in the present work, our final gaussian basis was taken to be $\text{Ca}(14s\ 9p\ 3d/9s\ 5p\ 3d)$, $\text{F}(9s\ 5p/4s\ 2p)$. All calculations referred to hereafter were carried out with the latter basis set.

The only nonstandard aspect of the present computations was the SCF procedure for the open shell $^1\text{B}_2$ state. For this purpose the methods developed by Hunt, Dunning, and Goddard²⁰ served admirably. Except for the SCF sections, the computer program used was a modified²¹ version of POLYATOM.²²

CONNECTION BETWEEN CALCULATIONS AND CHEMILUMINESCENCE

The first step in the calculations was, holding the bond angle at 150° , to predict the ground state Ca - F bond distance. A value of 3.854 bohrs = 2.039 Å was found and can be compared to the value 2.10 Å, obtained from electron diffraction experiments.²³ Using this predicted bond distance, we then proceeded to carry out SCF calculations for the 1A_1 , 1B_2 , and 3B_2 electronic states over a range of bond angles. These results are summarized in Table I and Fig. 2.

Perhaps the most unusual feature revealed in Fig. 2 is that the 3B_2 and 1B_2 states have rather small bond angles. However, this result is not entirely unanticipated, since Gole²⁴ has predicted the 3B_2 state of BeF_2 to have an equilibrium bond angle of 80° . Since the geometry of the 1B_2 state is closely tied to a simple explanation of the chemiluminescence experiments,³ eight additional calculations were carried out. These calculations predict the equilibrium geometry of 1B_2 CaF_2 to be $\theta = 54^\circ$, $R(Ca - F) = 4.059$ bohrs = 2.148 Å. This prediction is expected to be quite reliable, since both the bending and stretching force constants are substantial, i.e. the energy changes significantly when either bond distance or bond angle is changed. Note in Table I that our calculations predict the 3B_2 potential surface to be essentially congruent to the 1B_2 surface.

The predicted geometry of the 1B_2 state is consistent with Jonah and Zare's interpretation of their experiments. We draw this conclusion because a collision between an alkaline earth atom A and a halogen molecule X_2 is quite likely to pass through geometries rather near the 1B_2 equilibrium, namely short X-X distance and relatively long A-X distance. In fact, Jonah and Zare³ argue that the AX_2 molecule will execute a complex Lissajous motion about the

equilibrium geometry. Such a motion could never occur, for example, if the 1B_2 state were linear (${}^1\Sigma_u^+$) and inaccessible to $A + X_2$ collisions due to a barrier.²⁵

It should be pointed out that the present calculations also imply that the 1B_2 state is the first excited singlet state of CaF_2 . Inspection of the improved virtual orbital (IVO)²⁶ energies suggests that the $10a_1$ orbital is the only low-lying orbital not occupied in the SCF wave function for the ground state. Thus, in the simplest picture, the excited states of CaF_2 are formed by replacing each of the valence orbitals by $10a_1$, the lowest unoccupied orbital. More quantitatively, Fig. 3 gives a Walsh diagram,²⁷ or plot of orbital energies versus bond angle. All of the orbital energies except $10a_1$ were taken from the 1A_1 calculations, while the $10a_1$ orbital energy was taken from the 3B_2 calculations. Since the $6b_2$ orbital is the highest (of the ground state orbitals) occupied for all bond angles, simple molecular orbital theory predicts the 3B_2 state to be the lowest triplet state and the 1B_2 to be the first excited singlet. Walsh's rules²⁷ suggest that these two states should be much more bent than the ground state. Note that the $10a_1$ orbital energy decreases as the molecule is bent while the $6b_2$ orbital energy increases. Thus the promotion of an electron from a $6b_2$ to a $10a_1$ orbital results in a smaller bond angle. This of course is consistent with our ab initio results for the 3B_2 and 1B_2 states.

Since each of the $8a_1$, $3b_1$, $9a_1$, $5b_2$, and $1a_2$ orbital energies lies within 1 eV of $\epsilon(6b_2)$ for some angle, we expect additional excited states of CaF_2 of 3A_1 , 1A_1 , 3B_1 , 1B_1 , 3B_2 , 1B_2 , 3A_2 , and 1A_2 symmetry. Starting with ground state CaF_2 , these additional states may be thought of as arising from the promotion of an

electron from a $3\sigma_g$, $1\pi_u$, or $1\pi_g$ orbital of F_2 to the $4s$ orbital of Ca. All of these states should be more bent than the 1A_1 ground state, since the $8a_1$, $3b_1$, $9a_1$, $5b_2$, and $1a_2$ orbital energies increase from 180° to 75° . This simple argument is consistent with Gole's ab initio calculations²⁴ on BeF_2 , which he predicts to have a 3A_2 bond angle of 100° .

Additional information concerning the nature of the electronic states involved in $Ca + F_2$ collisions comes from Mulliken population analyses,²⁸ some of which are seen in Table I. The table shows that CaF_2 is indeed quite ionic in its ground state. The Ca atom does not have a charge of fully +2, but it is rarely the case in ab initio calculations that Mulliken populations are as large as the classical formal charges. Interestingly the CaF_2 ground state becomes somewhat less ionic as the molecule is bent. The 3B_2 and 1B_2 states of CaF_2 are seen to be just about one-half as ionic as the ground state. This of course supports our simple description of the ground state as $Ca^{++}F_2^{--}$ and the 3B_2 and 1B_2 states as $Ca^+F_2^-$. We also note that the $10a_1$ orbital near the equilibrium geometry for the 1B_2 state has a Ca population of 0.996 electrons and an F population of 0.002 electrons. Inspection of the wave function shows that the $10a_1$ orbital is roughly 67% Ca $4s$ and 30% Ca $4p$. The significant amount of $4p$ character is a bit surprising. Finally, the calculated electric dipole moments (Table I) also indicate that the 1A_1 state is much more ionic than the excited 3B_2 and 1B_2 states.

A point of obvious relevance to the chemiluminescence experiments is the $^1A_1 - ^1B_2$ energy separation. The equilibrium separation T_e between the two states is 0.19027 hartrees = 5.18 eV. Ideally, however, one would like to graphically display the entire potential surfaces for the two states in a way that would indicate the splitting for each possible CaF_2 geometry. In practice, of course,

it would be prohibitively expensive to generate the two surfaces ab initio. Two of the most obvious points at which to ask the ${}^1A_1 - {}^1B_2$ splitting are the equilibrium geometries of the two states. Near the expected ground state geometry ($R(\text{Ca} - \text{F}) = 3.854$ bohrs, $\theta = 150^\circ$), the energy separation is 0.2669 hartrees = 7.26 eV = 167 kcal/mole. Under single collision conditions, the ${}^1B_2 - {}^1A_1$ transition is more likely to occur near to 1B_2 equilibrium ($R(\text{Ca} - \text{F}) = 4.059$ bohrs, $\theta = 55^\circ$), where the splitting is only 0.04653 hartrees = 1.27 eV = 29 kcal/mole. Returning to the experimental BaCl_2 results, Jonah and Zare³ assign an emission from 2900 \AA (4.28 eV) to 6000 \AA (2.07 eV) to the transition between the Ba^+Cl_2^- -like excited singlet and the electronic ground state. The observed emission peaks at $\sim 4500 \text{ \AA} = 2.76$ eV, which agrees fairly well with the ab initio 1.27 eV Franck-Condon (vertical) transition from the 1B_2 state at its equilibrium geometry. When one realizes that the experiments were carried out on BaCl_2 and the computations on CaF_2 , it must be concluded that the mechanism put forward by Jonah and Zare is quite reasonable.

Finally, we carried out several calculations for the approach of Ca to F_2 . The F-F distance was frozen at 3.6843 bohrs, the equilibrium separation predicted for the 1B_2 state. The distances chosen from Ca to the F_2 center of mass were 3.617 , 5.617 , 7.617 , and 9.617 bohrs. Single configuration SCF calculations were performed for each of the three states of interest. These results are summarized in Fig. 4. Note that the CaF_2 covalent potential curve has been uniformly lowered by 0.133 hartrees. This reproduces the crossing point (8.98 bohrs) with the Ca^+F_2^- curve obtained from Coulomb's law. The necessity for such an empirical correction arises in part from the well-known²⁹

failure of the Hartree-Fock approximation to reproduce experimental electron affinities. Figure 4 is not intended to be a quantitatively correct picture of the interaction between Ca and F₂; its purpose is rather to show that the simple qualitative ideas discussed earlier are essentially correct. One specific point worth noting is that the Ca + F₂ curve is repulsive by ~ 0.3 eV when it is crossed by the Ca⁺⁺F₂⁼ curve. It should also be mentioned that these curves would be significantly altered if the F₂ equilibrium separation (2.68 bohrs) had been used. In reality of course, the F-F separation will be changing as the Ca atom approaches. However, the present calculations are not sufficiently reliable to justify an entire ab initio potential surface for CaF₂. Such a calculation³⁰ could be justified for BeF₂ if there were a significant probability that this system could be studied experimentally.

For completeness, a variety of CaF₂ properties are given in Table II. Note that the properties of the ¹B₂ and ³B₂ states are nearly identical.

ACKNOWLEDGMENTS

We thank Professors William H. Miller and Richard N. Zare for clarifying discussions. This research was supported by the National Science Foundation under Grant GP-31974.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

† Miller Fellow.

†† Alfred P. Sloan Fellow.

1. See, for example, J. C. Polanyi and J. L. Schreiber, "The Dynamics of Biomolecular Reactions", a chapter in Physical Chemistry-An Advanced Treatise, Volume VI, edited by H. Eyring, W. Jost, and D. Henderson (Academic Press, New York, 1972).
2. Ch. Ottinger and R. N. Zare, Chem. Phys. Letters 5, 243 (1970).
3. C. D. Jonah and R. N. Zare, Chem. Phys. Letters 9, 65 (1971).
4. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964).
5. E. F. Hayes, J. Phys. Chem. 70, 3740 (1966).
6. C. E. Moore, "Atomic Energy Levels", Nat. Bur. Std. (U.S.) Circ. No. 467, Vol. III (1958).
7. D. L. Hildenbrand, J. Chem. Phys. 52, 5751 (1970).
8. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, (Chapman and Hall, London, 1968).
9. R. S. Berry, Chem. Rev. 69, 533 (1969); R. Milstein and R. S. Berry, J. Chem. Phys. 55, 4146 (1971).
10. W. A. Chupka, J. Berkowitz, and D. Gutman, J. Chem. Phys. 55, 2724 (1971).
11. A. J. H. Wachters, J. Chem. Phys. 52, 1033 (1970).
12. E. Clementi, Tables of Atomic Functions, a supplement to IBM J. Res. Develop. 9, 2 (1965).
13. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results, (Addison-Wesley, Reading, Mass., 1972).

14. D. R. Yarkony and H. F. Schaefer, Chem. Phys. Letters 14, 000 (1972).
15. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
16. J. L. Gole, A. K. Q. Siu, and E. F. Hayes, to be published.
17. E. Clementi and D. L. Raimondi, J. Chem. Phys. 38, 2686 (1963).
18. V. Calder, D. E. Mann, K. S. Seshadri, M. Allavena, and D. White, J. Chem. Phys. 51, 2093 (1969).
19. D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 56, 5075 (1972).
20. W. J. Hunt, T. H. Dunning, and W. A. Goddard, Chem. Phys. Letters 3, 606 (1969); 4, 231 (1969); 6, 147 (1970).
21. N. W. Winter and R. M. Pitzer, unpublished.
22. D. Neumann, H. Basch, R. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and P. Liebmann, POLYATOM, Program 199, Quantum Chemistry Program Exchange, University of Indiana.
23. P. A. Akashin and V. P. Spiridonov, Soviet Phys.-Cryst. 2, 472 (1957).
24. J. L. Gole, to be published.
25. C. Maltz, Chem. Phys. Letters 9, 251 (1971).
26. W. J. Hunt and W. A. Goddard, Chem. Phys. Letters 3, 414 (1969).
27. A. D. Walsh, J. Chem. Soc. 2260, 2266, 2288, 2296, 2301, 2306 (1953).
28. R. S. Mulliken, J. Chem. Phys. 23, 1833, 1841 (1955).
29. E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964).
30. C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, Science, in press.

Table I. Self-consistent-field results for CaF_2 at a fixed Ca-F distance of 3.85409 bohrs

Total energy (hartrees)	45°	60°	75°	90°	120°	150°	165°	180°
1A_1	-875.50312	0.70644	0.76364	0.78958	0.81240	0.81927	0.81996	0.82006
3B_2	-875.58689	0.61796	0.59307	0.57286		0.55447	0.55559	0.55607
1B_2	-875.58583	0.61699	0.59206	0.57172	0.55336	0.55234	0.55339	0.55381
Mulliken Charges on Calcium Atom								
1A_1	+1.376	+1.424	+1.434	+1.468	+1.478	+1.480	+1.480	+1.481
3B_2	+0.775	+0.750		+0.710			+0.729	+0.728
1B_2	+0.778	+0.752		+0.712			+0.731	+0.731
Dipole Moment (debyes)								
1A_1	13.93	13.32	12.35	11.11		4.16		0.00
3B_1	4.50	3.92	3.24	2.61		0.27		0.00

Table II. Molecular properties of calcium difluoride. Unless indicated properties are given in atomic units^a

	$1A_1$	$3B_2$	$1B_2$
R(Ca-F)	3.85409	4.05908	4.05908
θ	150°	55°	55°
E(hartrees)	-875.81927	-875.62986	-875.62900
Ca Population	18.522	19.226	19.224
F Population	9.739	9.387	9.388
Dipole moment (debyes)	4.16	4.62	4.58
Quadrupole moment at calcium atom (10^{-26} esu. cm ²)			
θ_{xx}	16.60	8.00	7.97
θ_{yy}	-29.91	4.47	4.62
θ_{zz}	13.31	-12.48	-12.59
Electric field gradient			
q_{xx} (Ca)	-1.032	-0.694	-0.700
q_{yy} (Ca)	-1.032	-0.261	-0.267
q_{zz} (Ca)	2.064	0.955	0.968
q_{xx} (F)	-0.097	1.598	1.595
q_{yy} (F)	-0.097	-2.939	-2.941
q_{zz} (F)	0.194	1.341	1.346
q_{yz} (F)	0.000	-0.413	-0.385

(continued)

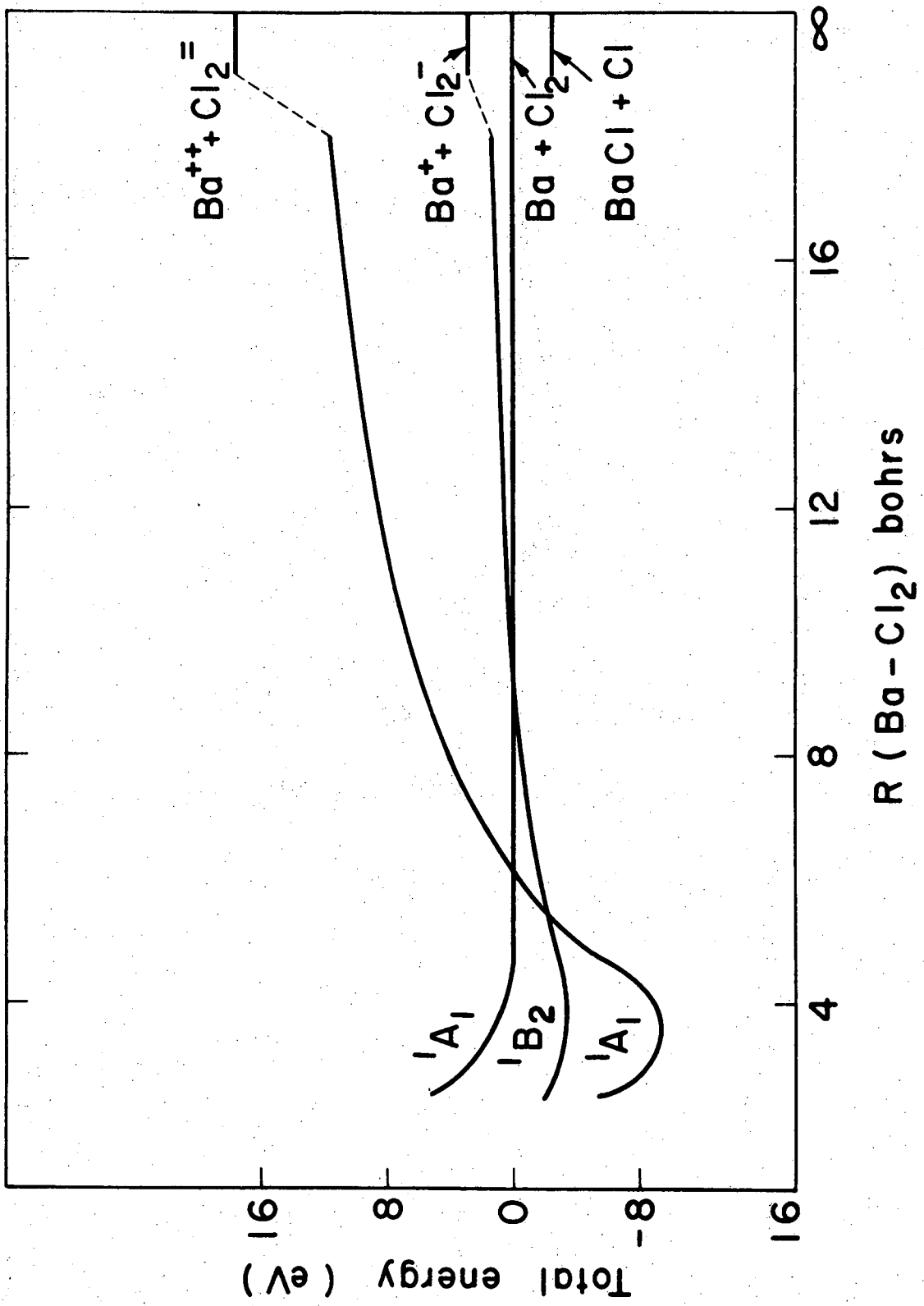
Table II. (continued)

	1A_1	3B_2	1B_2
Other properties			
$\langle 1/r_{Ca} \rangle$	84.870	84.620	84.621
$\langle 1/r_F \rangle$	33.127	33.930	33.930
$\langle r_{Ca}^2 \rangle$	336.252	370.138	370.119
$\langle r_F^2 \rangle$	861.615	516.465	516.562

^aSee S. Rothenberg and H. F. Schaefer, J. Chem. Phys. 53, 3014 (1970).

FIGURE CAPTIONS

- Fig. 1. Empirical potential curves for the perpendicular approach of a Ba atom to a Cl_2 molecule. The state symmetries indicated refer to C_{2v} geometry.
- Fig. 2. Total self-consistent-field energies of C_{2v} CaF_2 as a function of bond angle. The 3B_2 and 1B_2 curves are indistinguishable on the scale adopted.
- Fig. 3. Ab initio Walsh diagram for CaF_2 . The calculations were carried out for a Ca - F separation of 3.854 bohrs.
- Fig. 4. Ab initio potential curves for the approach of Ca to F_2 . Note discussion in text pertaining to the fact that the Ca + F_2 curve has been lowered by 0.133 hartrees.



XBL726 - 3153

Fig. 1

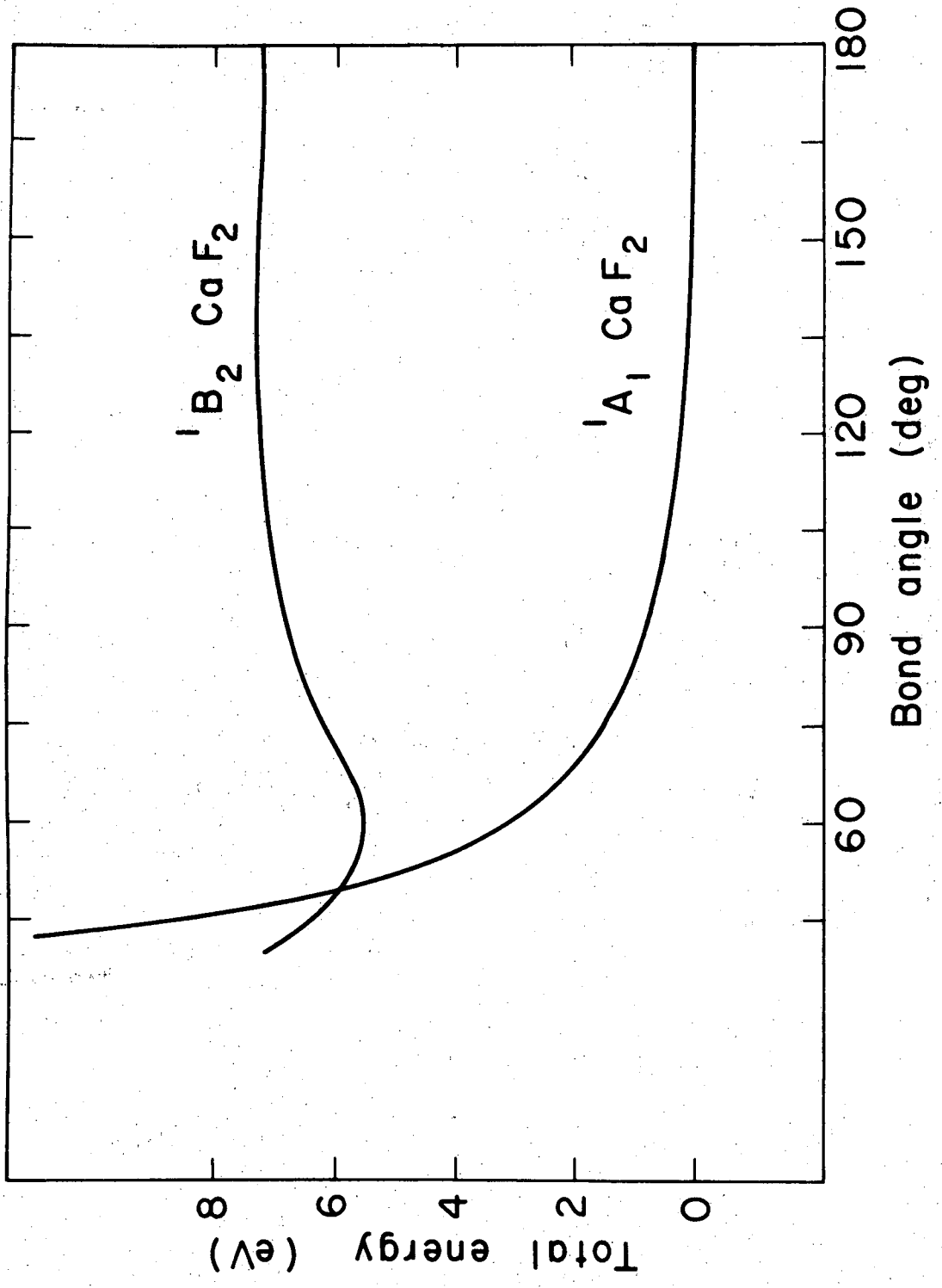


Fig. 2

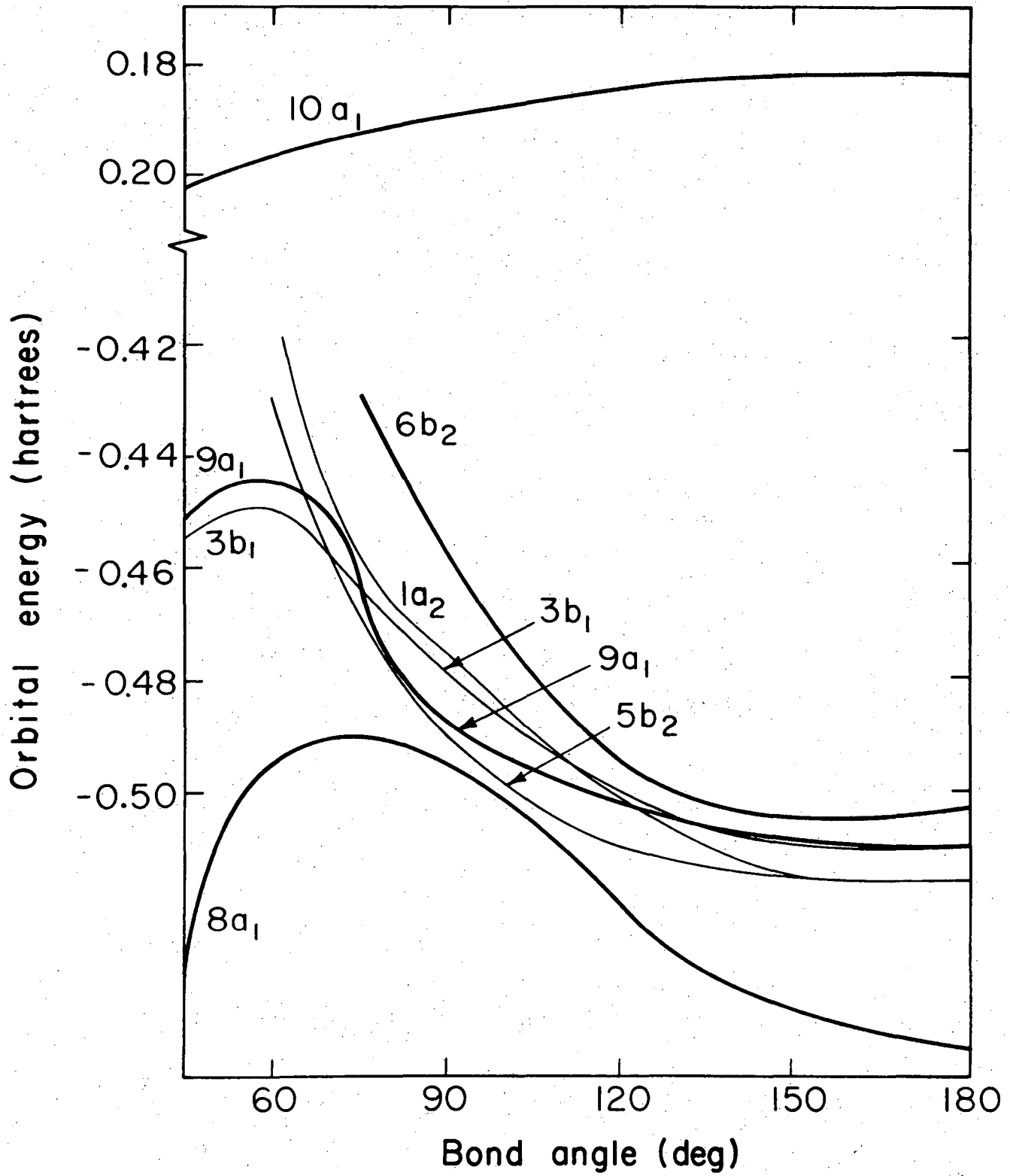
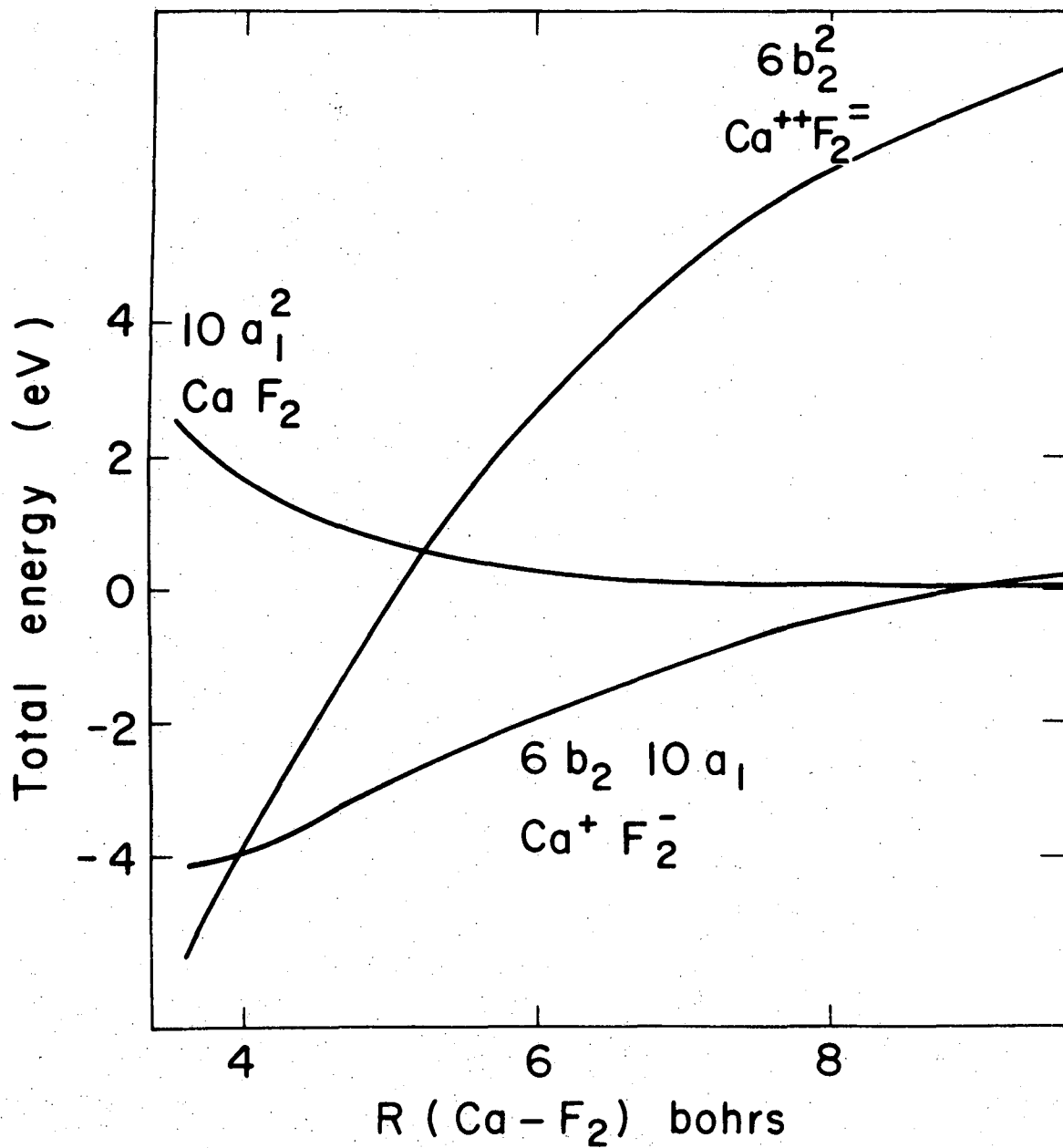


Fig. 3



XBL726-3155

Fig. 4

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720