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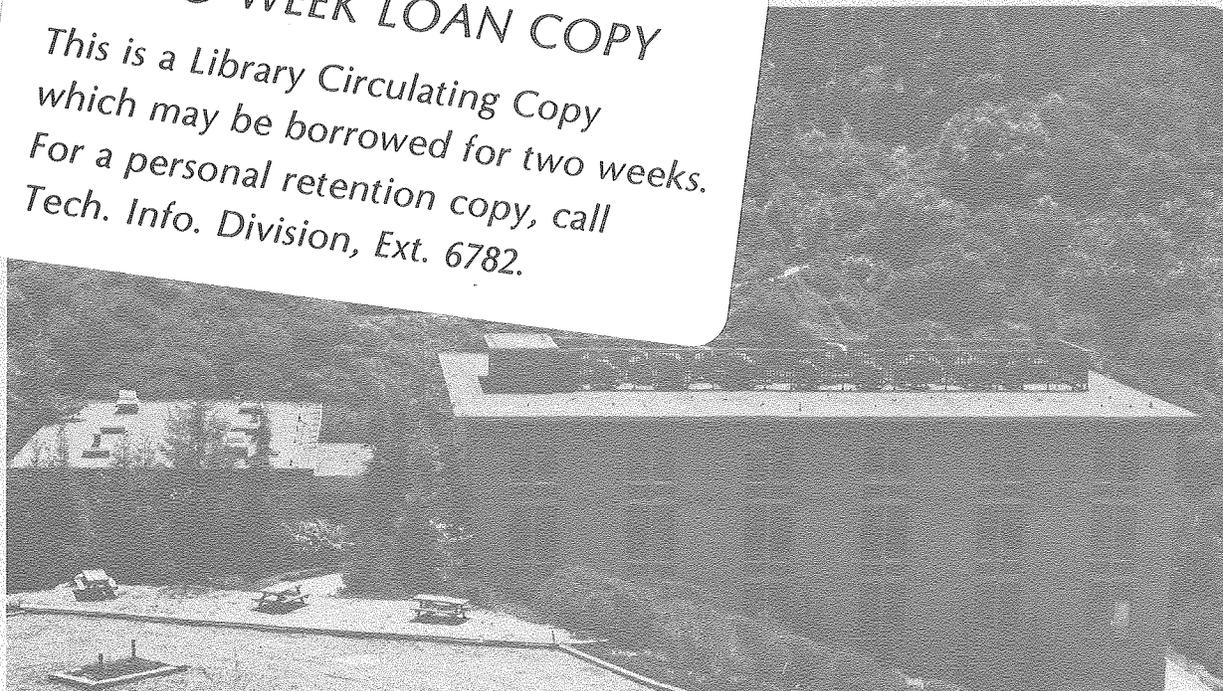
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III. BONDING IN THE ALKALINE EARTH DIATOMICS

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ANALYTIC POTENTIAL FUNCTIONS FOR WEAKLY BOUND  
MOLECULES. III. BONDING IN THE ALKALINE EARTH DIATOMICS.

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Abstract

The well regions of the weakly bound ground states of  $\text{Be}_2$ ,  $\text{Mg}_2$ ,  $\text{Ca}_2$  and  $\text{Sr}_2$  were analyzed in terms of the parameters of analytic potential functions. From this analysis, it is shown that bonding in these molecules is qualitatively different from that found in other molecules of similar binding energy. Bonding in  $\text{Be}_2$  is shown to be abruptly enhanced at  $R/R_e < 1.4$ , probably by substantial configurational mixing with  $2s2p$  character.

Be<sub>2</sub>, Mg, Ca<sub>2</sub> and Sr<sub>2</sub> are all weakly bound<sup>1-4</sup> due to the ns<sup>2</sup> configuration of the ground state atoms. The first excited configurations, nsnp and/or ns(n-1)d, lie considerably lower in energy than, for instance, in the rare gas atoms. These configurations are of importance to the proper description of large clusters of these atoms<sup>5</sup> and the bulk metals<sup>6</sup>. We inquire here into their role in diatomic bonding.

Our approach<sup>7-9</sup> is to analyze the interatomic potential in terms of the parameters of accurate, flexible analytic potential functions with readily interpretable parameters. We have inverted the spectroscopic constants<sup>2,3</sup> of the ground states of Mg<sub>2</sub> and Ca<sub>2</sub> to the potential constants of the Thakkar function<sup>10</sup>

$$V(R) = e_0 \lambda^2 \{1 + \sum_n e_n \lambda^n\} \quad (1)$$

where  $\lambda = 1 - (R_e/R)^p$  and p is a positive number. We have also obtained the Huffaker-Morse potential<sup>7,11</sup> constants for these two molecules. These various potentials are plotted in Fig.'s 1 and 2 for Mg<sub>2</sub> and Ca<sub>2</sub>, respectively. Also shown in these figures are the precise RKR potentials<sup>2,3</sup>. The parameters of the Thakkar potentials are given in Table I.

The Thakkar functions overestimate the dissociation energies of both molecules and fail to recover the correct long range behavior. The Huffaker-Morse functions are in somewhat better qualitative agreement with the RKR potentials. (The artificial maximum<sup>7</sup> in the analytic potentials at small R for Ca<sub>2</sub> is of less concern here). In contrast, we have found the Thakkar function to be quite accurate not only near R<sub>e</sub> but also at long range

for species with dissociation energies substantially greater than <sup>7</sup> (BeAr<sup>+</sup>,  $D_e \approx 4500 \text{ cm}^{-1}$ ), substantially less than <sup>8</sup> (NaAr,  $D_e \approx 42 \text{ cm}^{-1}$ ), and comparable to <sup>12</sup> (Ar<sub>2</sub>,  $D_e \approx 100 \text{ cm}^{-1}$  and XeF,  $D_e \approx 1175 \text{ cm}^{-1}$ ) those of Mg<sub>2</sub> and Ca<sub>2</sub>.

We turn now to Be<sub>2</sub>. There are no high resolution spectroscopic data on Be<sub>2</sub>; rather, we have used the ab initio calculation of the ground state reported by Liu and McLean<sup>1</sup>. There is good reason to believe that this calculation is quite accurate. A similar calculation of the Mg<sub>2</sub> potential<sup>13</sup> is in excellent agreement with the RKR potential at all internuclear distances. The qualitative features of the ab initio Be<sub>2</sub> potential are striking. The calculated well depth,  $800 \pm 80 \text{ cm}^{-1}$ , is nearly twice that of Mg<sub>2</sub>. The calculated internuclear separation,  $2.49 \text{ \AA}$ , is remarkably close to the nearest-neighbor separation in Be(s),  $2.24 \text{ \AA}$ .

We have fit the ab initio points for Be<sub>2</sub> to Thakkar potentials in two ways. The first used a spline interpolation among the ab initio points from which vibration and rotation constants ( $G_v$  and  $B_v$ ) were obtained. Mechanical spectroscopic constants were derived from these values, and the usual Thakkar inversion method was applied. This fit accurately reproduced the lower half of the potential well, but at  $R/R_e > 1.25$ , the Thakkar function exhibited an artificial maximum and slowly declined at larger  $R$  to an asymptotic value which was about one half the true well depth. A simpler fit was attempted in which the Thakkar well depth and  $R_e$  were constrained to the ab initio values, and  $p$  and  $e_2$  were systematically varied until a best least-squares fit to the ab initio points was obtained.

A comparison of this fit to the ab initio points is shown in Fig. 3. Again, the lower portion of the well is reproduced, but the tail at  $R/R_e > 1.4$  is decidedly different in shape. As must be the case, the ab initio points at large  $R$  reflect the

asymptotic  $R^{-6}$  attraction. What is striking is the persistence of this behavior for  $R/R_e$  as small as ca. 1.5. Near this distance, the shape of the attractive tail of the ab initio potential changes abruptly. To emphasize this behavior, the dashed curve in Fig. 3 is a very simple Thakkar function with  $p=5.69$ ,  $e_0=D_e=230 \text{ cm}^{-1}$ , and  $R_e=3.7 \text{ \AA}$  which was least-squares fit to the ab initio points beyond  $R/R_e=1.4$ .

Is this behavior the manifestation of a real, physical effect or is it simply an artifact of the functions used to fit the potential? We believe that the changes in shape of the curve is, in fact, due to a real change in the bonding characteristics of  $\text{Be}_2$  at  $R/R_e \approx 1.4$ . This change can be brought about if, at some distance, the ground state interaction finds it energetically favorable to admix a large  $2s2p$  character to the otherwise  $2s^2$  interaction. The  $2s2p$  interaction is decidedly bonding, but only at the expense of what would be called promotion energy in a valence bond description. That such an enhanced binding could occur in alkaline earths has been discussed previously,<sup>5,6,15,16</sup> but no accurate estimate of its magnitude had been available.

In Fig. 4, we plot the diatomic  $R_e$  versus the bulk nearest neighbor distances for Be, Mg, Ca and Sr. The relatively short  $\text{Be}_2$  bond is evident from this diagram. Extrapolation from the Mg, Ca, and Sr points would indicate that the  $\text{Be}_2$  bond should be ca. 3.4 to 3.5  $\text{\AA}$ , a range close to the 3.7  $\text{\AA}$   $R_e$  of the fit to the ab initio tail in Fig. 3. (The  $R_e$  for  $\text{Sr}_2$  is somewhat uncertain. Bergeman and Liao<sup>4</sup> estimate  $R_e(\text{Sr}_2)=4.50 \pm 0.2 \text{ \AA}$ . The lower limit, 4.3  $\text{\AA}$ , is the nearest neighbor distance<sup>14</sup> in  $\text{Sr}(s)$ , but, as Fig. 4 indicates,  $R_e=4.5 \text{ \AA}$  is in accord with the trend set by  $\text{Mg}_2$  and  $\text{Ca}_2$ .)

The ratio of the ab initio  $D_e$  to the  $D_e$  of  $Mg_2$  is 1.86. The corresponding ratio for the pair  $Li_2/Na_2$  is 1.46, and for  $B_2/Al_2$ , it is 1.96. Li and Be both have excited states derived from the first excited configuration at lower energies than corresponding excitations in Na and Mg, respectively. These comparisons further reinforce the picture of substantial configurational mixing in  $Be_2$  near  $R_e$ .

We now return to  $Mg_2$  and  $Ca_2$ . The failure of the Thakkar function to reproduce the RKR potentials of  $Mg_2$  and  $Ca_2$  is also due to a qualitatively different type of weak bonding from that found in, for instance, rare gas dimers. If the physical origin of the forces at long range is basically unaltered near  $R_e$ , then the Thakkar inversion is reliable from near  $R_e$  to large  $R$ , and  $p$  in Eq.(1) will be close to the leading exponent in an inverse  $R$  long range expansion.<sup>9</sup>

Being a property of the equilibrium position of the potential, one can calculate  $p$  values for any diatomic.<sup>9,10</sup> For chemically bound diatomics,<sup>17</sup> the average  $p$  is  $1.92 \pm 0.46$ . The smallest are for hydrides ( $1.29 \pm 0.21$ ), the largest are for halogens ( $2.52 \pm 0.22$ ), and the largest of these is for  $I_2$  (2.89). In contrast,  $p$  values for neutral rare gas containing diatomics range from 4.31 (NaAr) to 5.62 ( $Ar_2$ ) to  $\sim 6.5$  (XeF), values which are typical of each homologous series.

From Table I,  $p=3.59$  and  $3.56$  for  $Mg_2$  and  $Ca_2$ , respectively. These intermediate values of  $p$  are measures of the differences in equilibrium bonding in those molecules in comparison to other molecules of similar  $D_e$ . We also note that the Huffaker-Morse function gives (empirically) a better represent-

ation of strong, chemically bound diatomic potentials than does the Thakkar function.  $Mg_2$  and  $Ca_2$  thus appear to be incipiently covalent, at least to the extent that one measures such a concept by the shape of the interatomic potential near  $R_e$ . As measured by bond lengths and energies,  $Mg_2$  and  $Ca_2$  are not influenced by excited configurations to the extent that  $Be_2$  is, but there is clearly significant participation from such configurations.<sup>18</sup>

This analysis also reinforces the predictions<sup>5,15</sup> that  $Ba_2$ , while still rather weakly bound, will have a short bond length due to the interaction with low lying 6s6p and 6s5d configurations. Due to the numerous isotopes of Ba and a rotational constant of ca.  $0.013 \text{ cm}^{-1}$  for  $Ba_2$  with  $R_e \sim 4.4 \text{ \AA}$  (the Ba(s) contact distance), direct spectroscopic verification of this prediction will be extraordinarily difficult.

Although the spectroscopic constants<sup>4</sup> for  $Sr_2$  are less precise than those for  $Mg_2$  and  $Ca_2$ , these constants indicate that the bonding in  $Sr_2$  is not very different near  $R_e$  from that of  $Mg_2$  or  $Ca_2$ . Bergeman and Liao<sup>4</sup> interpreted their photoluminescence spectra in terms of a simple Morse function for the ground state potential. One can obtain a value for the reduced curvature at  $R_e$ ,

$$\kappa = \frac{R_e^2}{D_e} V''(R_e) = \frac{\omega_e^2}{2 B_e D_e}$$

Their data yield  $\kappa = 38 \pm 4$ . For a Morse function<sup>9</sup>,  $\kappa = 2(p+1)^2$ , implying  $p = 3.35 \pm 0.23$ , in close accord with  $Mg_2$  and  $Ca_2$ . (The reduced curvatures of  $Mg_2$  and  $Ca_2$  are 32.65 and 41.92, respectively).

In conclusion, we have used analytic potential function fits to demonstrate the quantitative differences in bonding

among the alkaline earth diatomics themselves. In the vicinity of  $R_e$ ,  $Mg_2$ ,  $Ca_2$  and  $Sr_2$  appear to have quite similar potentials, implying a common mechanism for bonding which is somewhat enhanced over that found in rare gas containing diatomics (with the likely exception<sup>12</sup> of XeF). These molecules are to be contrasted to  $Be_2$  where, even at the dimer level, a noticeable bond shortening and abrupt change in the shape of the potential function indicates quite clearly the significant role of excited state participation in what is nevertheless a very weak bond.

It is at least as difficult to apply the term "van der Waals bond" to a molecule as it is to apply the terms "ionic bond", "covalent bond", or any of a host of other terms. It is clear that bond energy alone is an insufficient criterion by which to make such classifications and that even the weakest of interatomic bonds show considerable diversity when these bonding interactions are fully analyzed.

#### Acknowledgement

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18. Hence an extrapolation in Fig. 4 from Sr, Ca, and Mg to Be gives  $R \approx 3.4 \text{ \AA}$  for  $\text{Be}_2$ , rather than the  $3.7 \text{ \AA}$  value of the dashed potential shown in Fig. 3.

Table 1. Thakkar potential constants for  $\text{Mg}_2 \text{X}^1\Sigma_g^+$  and  $\text{Ca}_2 \text{X}^1\Sigma_g^+$ . Standard errors refer to the last digits.

	$\text{Mg}_2$	$\text{Ca}_2$
$R_e$	3.88941(15) Å	4.2785227 (46) Å
$e_o$	545.6 (2.9) $\text{cm}^{-1}$	1812.74 (.52) $\text{cm}^{-1}$
$p$	3.5897 (95)	3.55688 (51)
$e_1^a$	0	0
$e_2$	0.0620 (48)	-0.25518 (31)
$e_3$	0.0777 (92)	-0.39506 (33)
$e_4$	-0.119 (13)	-0.43595 (45)
$e_5$	-0.104 (20)	1.0613 (75)
$e_6$	0.052 (25)	-1.14370 (96)
$D_e$ (Function)	528.7 (42.2) $\text{cm}^{-1}$	1274.9 (33.3) $\text{cm}^{-1}$
$D_e$ (expt) <sup>b</sup>	430±1 $\text{cm}^{-1}$	1095±0.5 $\text{cm}^{-1}$

<sup>a</sup>  $e_1$  is identically zero by our choice for  $p$ . See Ref. 7-10.

<sup>b</sup> Experimental values from Ref.'s 2 and 3, respectively.

### FIGURE CAPTIONS

- Fig. 1.* Potential functions for  $Mg_2$ . The solid line is the RKR potential from Ref. 2. The analytic function fits are the Thakkar function (--) and the Huffaker-Morse function (---).
- Fig. 2.* Potential functions for  $Ca_2$ . The solid line is the RKR potential from Ref. 3. The analytic functions are denoted as in Fig. 1.
- Fig. 3.* Ab initio potential points ( $\odot$ ) for  $Be_2$  (from Ref. 1) compared to a Thakkar function fit to the well region (solid line) and the long-range tail (dashed line).
- Fig. 4.* The  $Be_2$ ,  $Mg_2$ ,  $Ca_2$  and  $Sr_2$  bond lengths ( $R_e$ ) plotted versus the nearest-neighbor separations in solid Be, Mg, Ca, and Sr ( $R_m$ ).

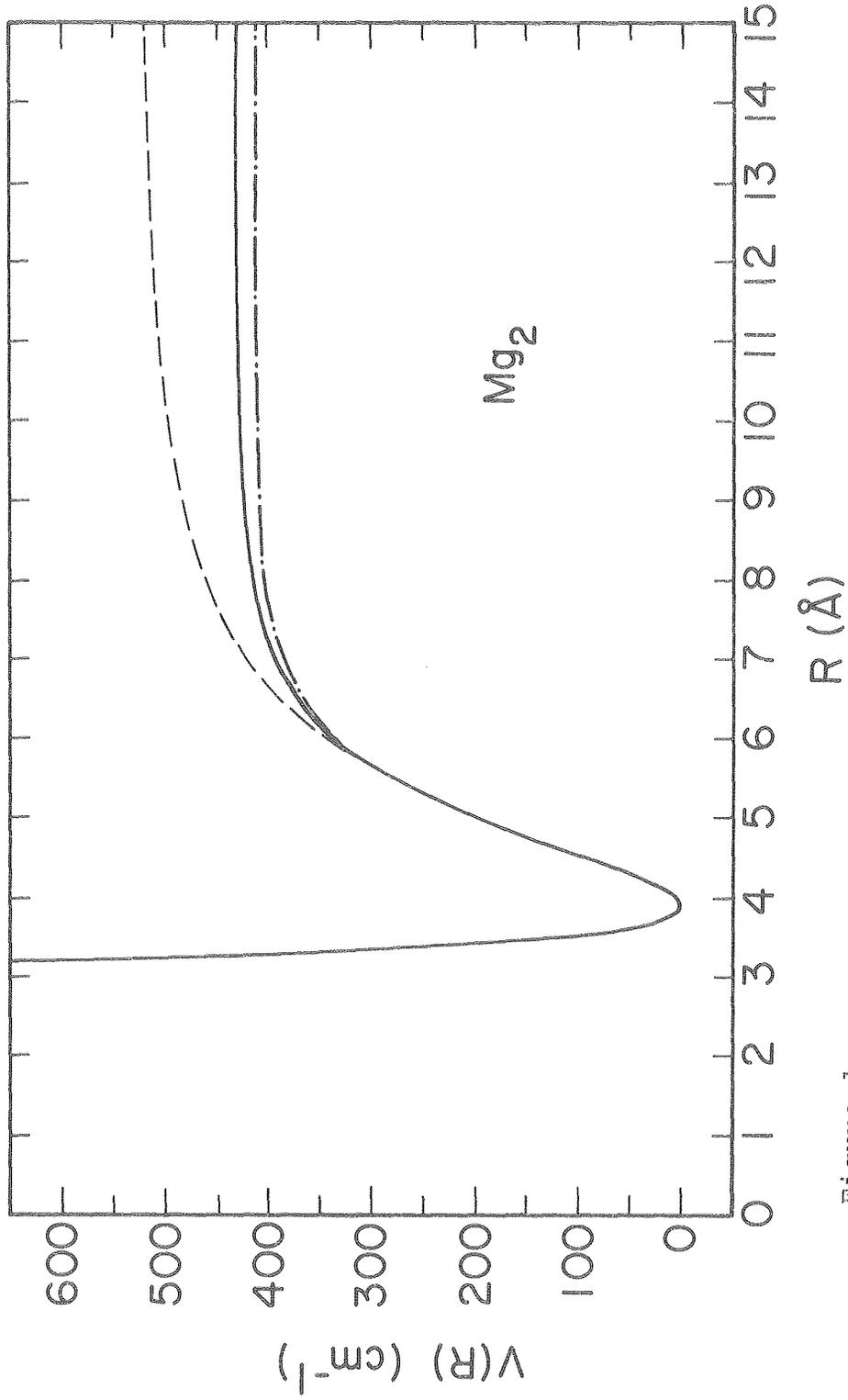


Figure 1

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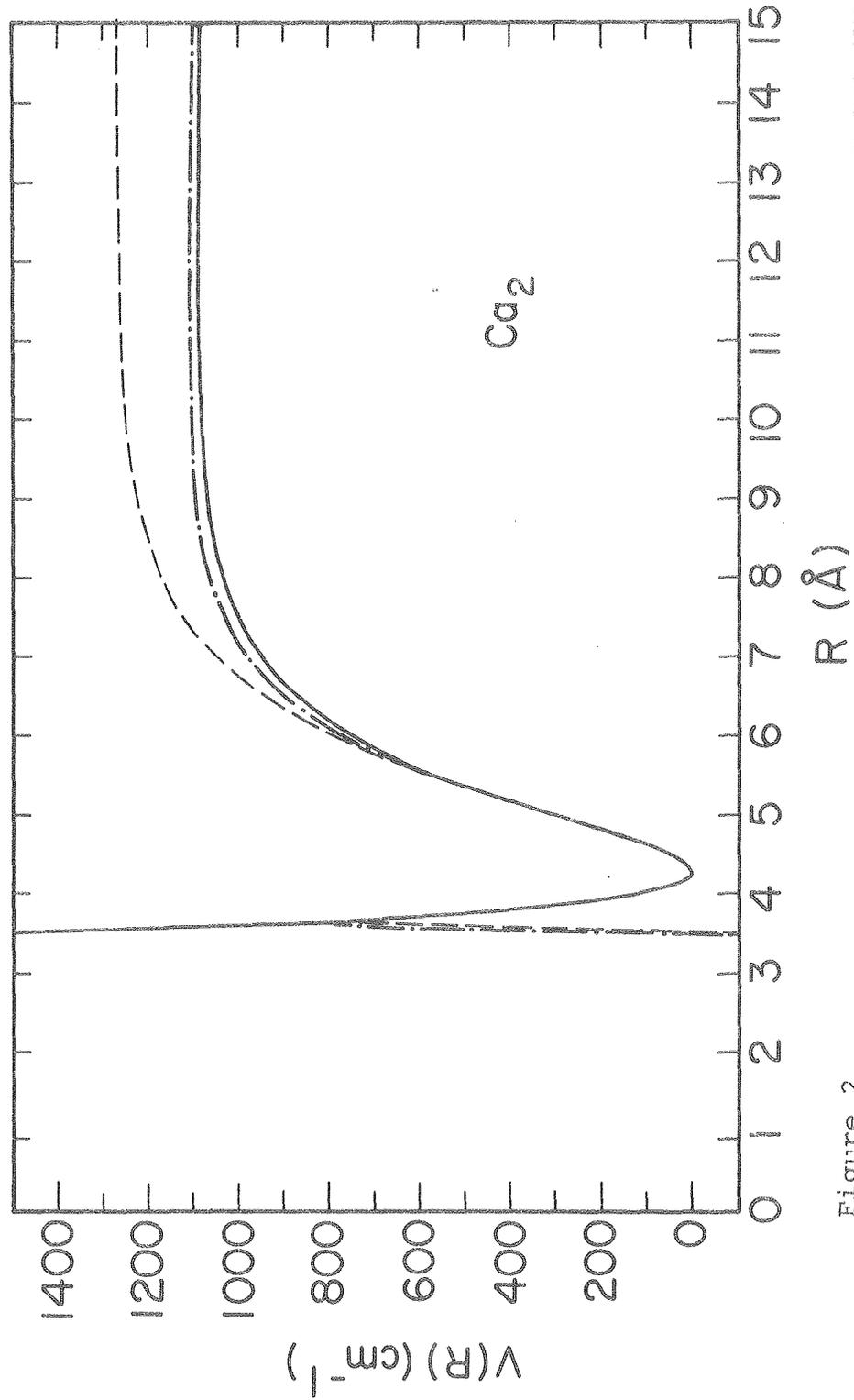


Figure 2

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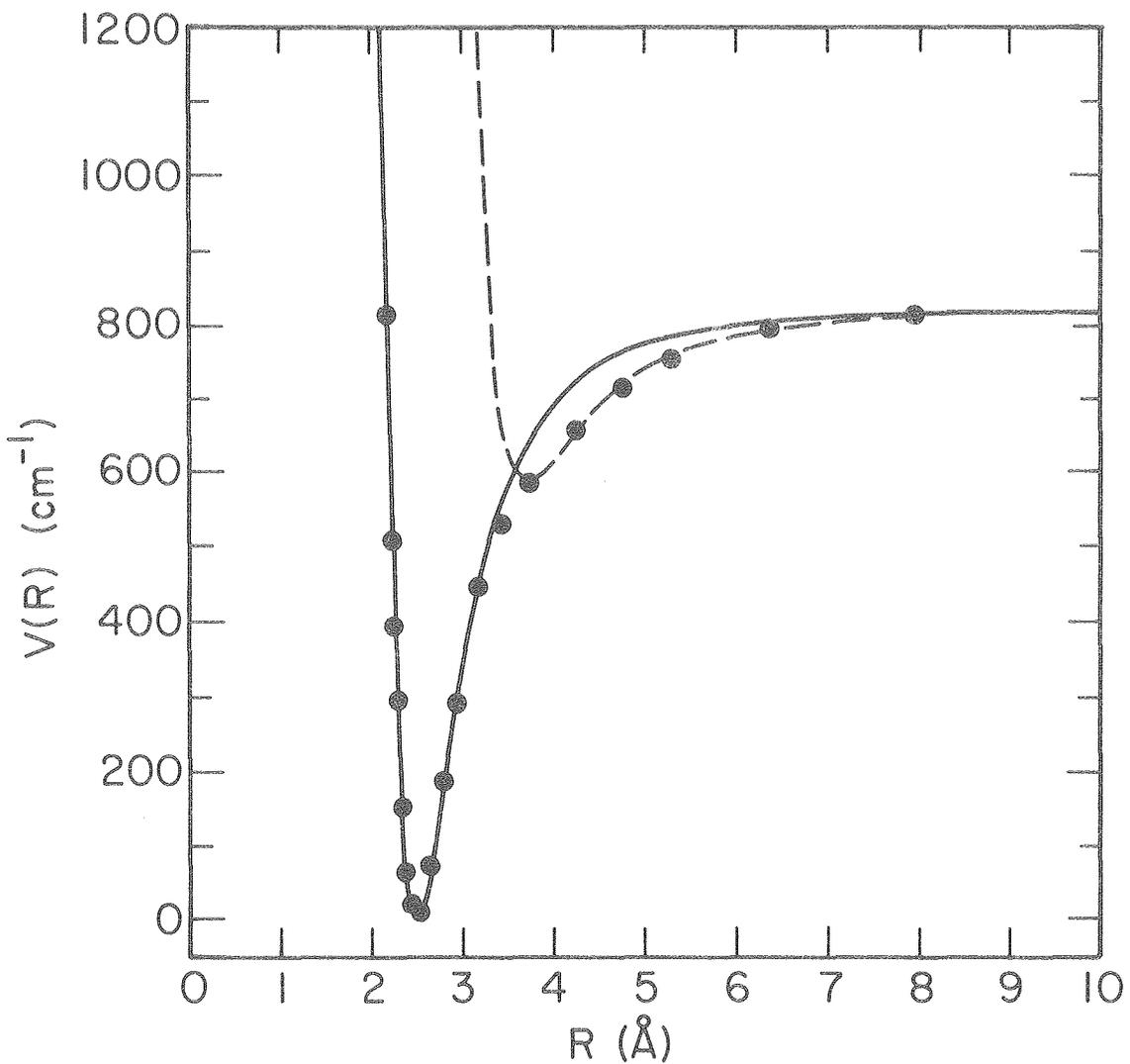


Figure 3

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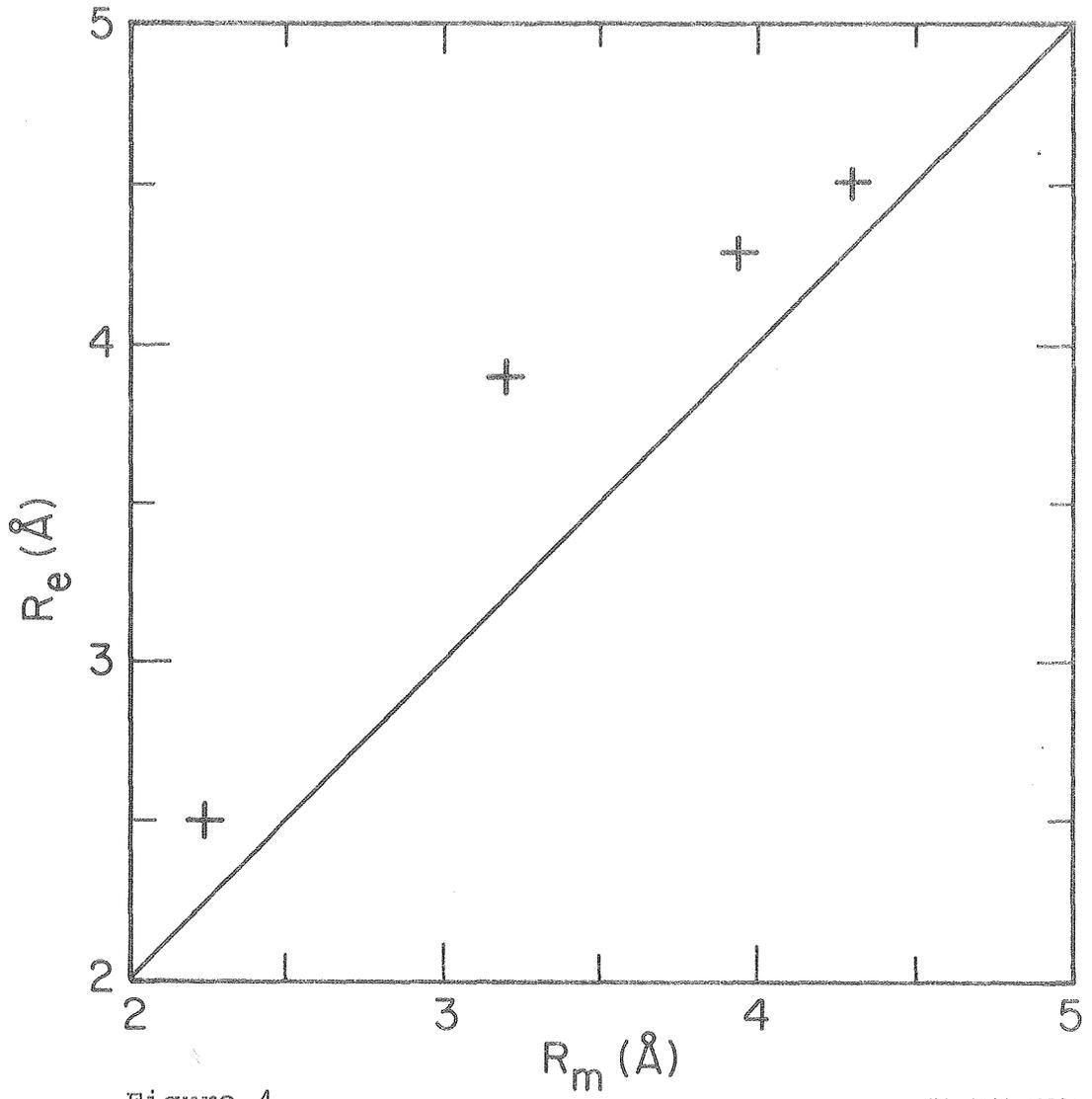


Figure 4

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