Ca_2: a van der Waals Molecule

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Summary Spectral studies on calcium vapour indicate that the Ca_2 molecule is bound in its $^1\Sigma_g^+$ ground state, with an equilibrium bond length of 0·428 nm, a vibrational frequency $\omega_e'' = 65{\cdot}0_9$ cm^{-1}, and a dissociation energy $D_0'' = 940 \pm 40$ cm^{-1}.

THE question of whether or not dimeric species are present in the vapours of the alkaline-earth metals has been the subject of conjecture for a considerable time. In **1931** Hamada[1] examined the spectra of Mg and Ca among others, in emission from a hollow-cathode lamp. The asymmetric broadening of the respective resonance lines and flutings observed to the red of the resonance lines suggested the presence of "quasimolecules". Two recent papers on calcium have lent some support to Hamada's interpretation. The profile of the 422·7 nm ^1P–^1S atomic absorption line of calcium was shown[2] to be dependent upon the square of the calcium pressure and the fluted absorption in the 430—530 nm range was found[3] to be discrete and many-lined.

We have re-examined at high resolution the absorption spectrum from calcium vapour in a King furnace at 2300K. Plates were taken in the 11th and 12th orders of a 10 m vacuum Ebert spectrograph at the Division of Physics, National Research Council of Canada, Ottawa. Rotational and vibrational analyses assign the many-line spectrum to Ca_2 unambiguously.

The transition is identified as $^1\Sigma$–$^1\Sigma$ type in agreement with the predictions of simple molecular orbital theory. The Ca_2 molecule has a total of 40 electrons and the ground-state electron configuration,

(a) KKLLMM $(\sigma_g 4s)^2(\sigma_u 4s)^2$

gives rise to a $^1\Sigma_g^+$ molecular state. The lowest-energy excited-state configuration is

(b) KKLLMM $(\sigma_g 4s)^2(\sigma_u 4s)(\sigma_g 4p)$

which gives rise to a $^1\Sigma_u^+$ (and a $^3\Sigma_u^+$) electronic state.

As molecular electron configuration (a) has an equal number of bonding and antibonding electrons no formal chemical bond would be expected. However, the experimental evidence shows that Ca_2 is weakly bonded at large internuclear distance in its ground state. The bonding can be attributed wholly to van der Waals interaction between the two Ca atoms.

The principal constants for the ground state of the molecule, based on 249 levels involving five vibrational states, are

$$\omega_e'' = 65{\cdot}0_9\ \text{cm}^{-1}; \qquad \omega_e x_e'' = 1{\cdot}11\ \text{cm}^{-1}$$
$$B_e'' = 0{\cdot}0460\ \text{cm}^{-1}; \qquad r_e'' = 0{\cdot}428\ \text{nm}.$$

By extrapolation we estimate the dissociation energy D_0'' to be 940 ± 40 cm^{-1}. The absolute vibrational numbering in the $A\,^1\Sigma_u^+$ state is not known but information from the v'–0 progression is given in the Table.

The situation in calcium is thus analogous to that already observed for magnesium[4] where the transition is from a very lightly bonded ground state to a more stable excited state. The greater well-depth for Ca_2 over Mg_2 in the ground state, *ca.* 970 cm^{-1} as against 424 cm^{-1}, is probably due to the greater polarisability and lower electron promotion energy of the Ca atom.

It is possible to derive potential energy curves from spectroscopic data and the study of the Group IIA diatomic molecules provides a route to accurate data on long-range van der Waals forces. Such data from Mg_2 have proved extremely useful in testing theoretical calculations[5] in this area and it is hoped that the information on Ca_2 will prove equally so. A fully documented account of the analysis of the Ca_2 spectrum will be published elsewhere.

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TABLE

Data from the v'–0 *progression in the* $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ *system of* Ca_2

Band	ν_0 (cm^{-1})	B_v' (cm^{-1})	$D_v' \times 10^8$ (cm^{-1})
v–0	19401·0	0·0571	4·5
$(v+1)$–0	19531·7	0·0568	4·5
$(v+2)$–0	19661·0	0·0564	4·6
$(v+3)$–0	19788·6	0·0561	4·7
$(v+4)$–0	19914·5	0·0557	4·8
$(v+5)$–0	20038·8	0·0554	5·0
$(v+6)$–0	20161·4	0·0550	5·0

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