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Does He_2 Exist?

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For the electronic ground state $X\,^1\Sigma_g^+$ the potential-energy function of He_2 reported by Aziz et al. has been transformed into the form V(z), containing only eight parameters, which is more suitable for the investigation of the existence of states of discrete energy. We found no evidence that a bound vibration-rotational state of the stable diatomic molecule $^3He_2$ or $^4He_2$, even if rotating, can exist in the electronic ground state.

Neutral diatomic molecules in their electronic ground states exist with dissociation energies varying from relatively large, such as CO which is found even in the outer solar atmosphere in which the temperature is ~5000 K, to small, such as the molecules of the noble-gas elements Ne_2, Ar_2 etc. The spectral dissociation energy D_0 (conventionally expressed in wavenumber units) is defined to be the minimum energy necessary to take the molecule from the ground vibration-rotational state (specified by quantum numbers $v = 0$ and $J = 0$) in the electronic ground state to the states of continuous energy above the dissociation limit for the neutral atoms in their electronic ground states. For Ar_2 the process

$$^{40}Ar_2\,(X\,^1\Sigma_g^+, v = 0, J = 0) \rightarrow 2\,^{40}Ar\,(^1S_0) \qquad (1)$$

requires only $D_0 = 9956\ m^{-1}$, equivalent to 1.98×10^{-21} J per molecule or 1190 J mol^{-1} of the diatomic molecule;[1] because this energy is only about half the mean thermal energy at 300 K, Ar_2 is mostly dissociated under ambient conditions. Nevertheless the absorption spectrum of gaseous Ar under appropriate conditions has proved the existence of the diatomic molecules in stable discrete states.[1] The molecular species Ne_2 also exists but its dissociation energy is smaller than that of Ar_2. The question arises whether the He_2 diatomic molecule in its electronic ground state can formally exist.

From a classical point of view, as any two neutral atoms approach each other along the line of their centres from a distance R larger than their effective diameters, the potential energy decreases. In the absence of stronger forces, the consequent attraction is attributed to dispersion forces, first characterised by London.[2] At a still smaller distance comparable with the effective atomic diameter, the energy reaches a minimum and increases on further approach. The existence of such a minimum of energy (at a distance denoted R_e) is a necessary condition for a stable molecule but an insufficient condition. An additional requirement is that at least one stationary state exists having total energy less than that at the dissociation limit. If any such bound state exists, then the corresponding state with the least energy is the stationary state characterised by the conditions $v = J = 0$, signifying only the zero-point energy. The equilibrium binding energy is the energy at the dissociation limit that we denote D_e, relative to the zero of energy taken at the minimum at which the internuclear separation is R_e. The formal condition for stability is that $D_0 > 0$.

The prospectively most accurate method to determine the potential-energy function of a diatomic molecule in the region of the bound molecular states requires the inversion of spectral data, specifically the data for the vibration-rotational energies even if the spectra involve electronic transitions. In the case of He_2, no discrete spectrum involving the electronic ground state has been reported. Other means of determining the potential energy of pairwise interaction of two atoms at distances over a broad range and including information about the energies both above and below D_e have however been developed from diverse experimental data for the gaseous, liquid and solid states of aggregation.[3] With such a known potential-energy function it is practicable to calculate the energies of possible vibration-rotational states. Our implementation of this procedure for He_2 is what we here report.

The internuclear potential-energy function claimed to be most accurately determined from experimental data is that due to Aziz et al.[4] These workers deduced the existence of an extremely weakly bound state, in fact only one for $^4He_2$ and none at all for $^3He_2$. In the former case the dissociation energy was stated to be "1.684 mK" or 0.117 m^{-1}, equivalent to one part in ~ 10^4 relative to D_e, but with estimate given explicitly of neither its precision nor accuracy.[4] Because the experimental data on which this potential-energy function is based have relative uncertainties in the range 0.1-4.7 per cent,[4] the specification of such a small value for the dissociation energy, especially nominally carrying four significant digits, seems questionable. For this reason we have investigated an alternative approach to discover the existence of any bound state.

Aziz et al. represented the potential energy in the form[4]

$$V(R)/m^{-1} = 760.9\{1.84431 \times 10^5 \exp[-10.4333R/R_e - 2.27965(R/R_e)^2] - f(R)[1.367(R_e/R)^6 + 0.4212(R_e/R)^8 + 0.1747(R_e/R)^{10}]\} \qquad (2)$$

in which $R_e = 2.963 \times 10^{-10}$ m, $f(R) = \exp[-(1.4826R_e/R - 1)^2]$ if $R < 4.393 \times 10^{-10}$ m and $f(R) = 1$ otherwise. (Further digits, although not significant, that were specified by Aziz et al. were carried through our calculations.) We transformed this potential energy into the form more useful for spectroscopic purposes,[5,6]

$$V(z) = c_0 z^2(1 + \sum_{j=1} c_j z^j) \qquad (3)$$

in which $z \equiv 2(R-R_e)/(R+R_e)$. The vibration-rotational energies of a diatomic molecule in an electronic state of type $^1\Sigma$ may within some range be accurately represented in the form[7]

$$E(v,J) = \sum_{k=0} \sum_{l=0} Y_{kl}(v+1/2)^k[J(J+1)]^l; \qquad (4)$$

Table. 1. The Values of R_e and the Coefficients c_j in the Potential-Energy Function of He_2 in the Electronic Ground State X $^1\Sigma_g^+$

j	c_j
0	28877.60±0.64 m^{-1}
1	-5.634692±0.000090
2	16.8064±0.00089
3	-32.0265±0.0060
4	40.297±0.020
5	-32.440±0.033
6	15.125±0.028
7	-3.1009±0.0090
	$R_e/10^{-10}$ m = 2.963

the term coefficients Y_{kl} therein depend explicitly on the parameters c_j, $0 \leq j$, in the function V(z) and implicitly on R_e.[5] As many coefficients c_j are taken as are required, or as can be significantly determined, for a given purpose.[6] The expressions for Y_{kl} containing the coefficients c_j up to j = 10 have been published,[8] and further expressions containing c_j up to j = 16 have been generated according to the hypervirial perturbation method.[9] Because the function (2) is only piecewise continuous, its transformation to the form (4) by means of repeated analytic differentiation is impracticable; for this reason we used a procedure of numerical fitting according to the criterion of the least squares of the residuals. The best fit, consisting of only eight parameters c_j, $0 \leq j \leq 7$, listed in the table, was obtained for points at 110 selected geometrically increasing intervals (the factor was 1.010) in the range/10^{-10} m [2.5, 7.4]; the standard deviation of the fit was only 0.01649 m^{-1}, much smaller than the accuracy that might be claimed for equation (2). The range of the fit encompasses a broader region than that in which the potential energy V(R) is less than the equilibrium binding energy D_e, as shown in the figure. Other fits containing more numerous parameters made over the regions of $R/10^{-10}$ m [2.0,7.2] and [2.0,20.6] produced larger standard deviations and consequently larger estimated standard errors of parameters. Nevertheless, all the successful fits produced curves indistinguishable from both that in the figure and that of equation (2). On the basis of these parameters c_j in the table, according to equation (4) we have produced an estimate (785.5 ± 4.5) m^{-1} for the putative state of zero-point energy v = J = 0 of $^4He_2$; this value exceeds significantly the equilibrium binding energy D_e =

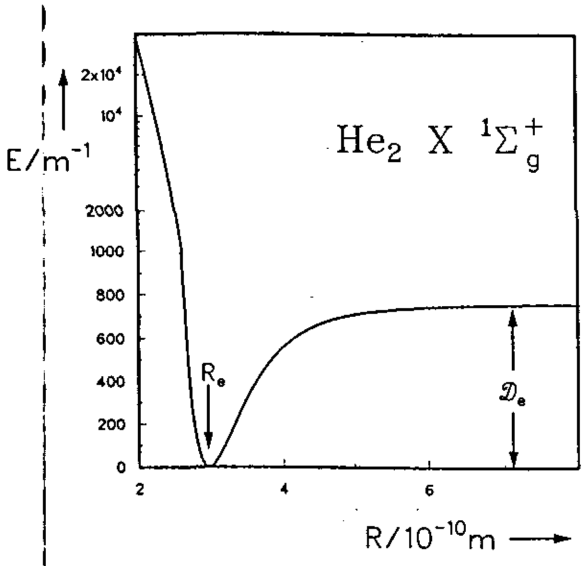

Fig. 1. The potential-energy function of He_2 in the electronic ground state; the ordinate scale is linear in the range E/m^{-1} [0,1000] and logarithmic thereabove.

760.9 m^{-1} (having no uncertainty stated by Aziz et al.[4] but roughly confirmed by subsequent computations[10]).

The use of equation (4) requires justification. Although for other molecules this equation has proven applicable up to 99.96 per cent of the dissociation limit,[11] because of the relatively small reduced mass of even $^4He_2$ the convergence of equation (4) is expected to be problematical before such an approach to the energy at D_e. However for HF which has an even smaller reduced mass, equation (4) has been demonstrated to be quantitatively accurate up to 63 per cent of D_e.[12] Indeed we observed the effects of such lack of convergence; the second-order contributions to $Y_{1,0}$ and $Y_{2,0}$ were about 2.5 and 1.5 per cent of the leading terms respectively, although the terms in the further contribution $Y_{0,0}$ to the zero-point energy were much less than one per cent of $Y_{1,0}$ and indeed tended to cancel one another. Consistent with a robust fitting procedure, the values of the parameters c_j from other fits are remarkably similar to those in the table up to and including c_4, although differences naturally arise in the higher coefficients because of the varied extent of truncation of the power series in equation (3). Thus the function V(z), which has been already demonstrated to be a useful representation of the potential energy of Ar_2,[5] is here confirmed to be a compact and accurate form also for He_2. In fact the nine parameters, including R_e, of which the values are given in the table number equally to those used by Aziz et al. in their empirical form which unnecessarily complicates the investigation of such spectral properties as the location of discrete states if any exists.

We also examined whether a centrifugal contribution to the potential energy might lead to a stable state. For this purpose, to the internuclear potential energy in equation 3 we added the rotational term $hJ(J+1)/(8\pi^2 c\mu R^2)$. The results showed that, although the potential-energy curves for $J = 1$ and $J = 2$ had true minima, the curve for $J = 3$ shows only metastability; the minimum energy near 3.1×10^{-10} m exceeds the energy at the dissociation limit as $R \rightarrow \infty$, with an energy maximum in between. For the values $J \geq 4$, the curves entirely lack a minimum. Furthermore, even for the curves for $J = 1$ and $J = 2$ the depth of the energy well is less than for that of the curve for $J = 0$, because the energy at the minimum of the well rises more rapidly with increasing values of J than the centrifugal barrier. Therefore even a tangential approach of one He atom to another appears to be unable to lead to a stable or discrete state of the diatomic molecule.

In conclusion, according to the use of powerful spectroscopic methods, we have found no evidence for the existence of any vibration-rotational bound state for $^4He_2$ in its electronic ground state. Our results demonstrate quantitatively that no bound state exists below two thirds the equilibrium binding energy D_e, and indicate further at least qualitatively that no bound state exists before D_e. Although with the present accuracy we cannot exclude entirely the possibility that a bound state exists, the value of the dissociation energy "$D_0 = 1.684$ mK" alleged by Aziz et al. is certainly not nearly so accurate as they imply.[4] We agree however that $^3He_2$ is much less likely than $^4He_2$ to have any discrete state in the electronic ground state.

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Key Words

Potential-energy function; Stability of He_2 molecule.

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