Volume 86, number 2 CHEMICAL PHYSICS LETTERS 12 February 1982

THE GROUND-STATE H_3 MOLECULE

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Received 18 November 1981

Nuclear dynamical calculations have been performed on the H–H_2 van der Waals molecule. An analytic estimate of the anisotropic potential has been derived and several isotropic potentials tested. For a well depth of 17 ± 2 cm^{-1} H_3 is found to have a weakly bound state at -0.12 ± 0.05 cm^{-1}. Isotopic substitution has been investigated: D_3 is found to have several bound states.

1. Introduction

The H_3 system has excited much interest both theoretically [1] and experimentally [2]. In particular it has been used to study elastic, inelastic and reactive scattering. The H_3 molecule has been observed in an excited Rydberg state [3], a finding confirmed by ab initio calculation [4,5], but as yet we know of no experimental evidence for it in its electronic ground state.

The ground-state potential energy surface of H_3 has been much studied, especially in the region of the activation barrier of the hydrogen exchange reaction. In particular, the calculations of Siegbahn and Liu [6,7] are to within chemical accuracy (4 kJ mol^{-1}). However, these calculations concentrate on the repulsive region of the potential relevant to the exchange process and do not extend into the region where there is a shallow van der Waals minimum. Recently Varandas and Tennyson [8] have successfully interpolated between these short-range calculations and the asymptotically correct, long-range multipolar expansion to give an isotropic potential in the region of the van der Waals minimum. They also studied the anisotropic terms at small separations, but lacked the anisotropic multipolar coefficients to give a full anisotropic potential. From their results it is however possible to obtain an estimate of the leading anisotropic (V_2) term in the Legendre polynomial expansion of the potential

$$V(R,r,\theta) = V_0(R,r) + V_2(R,r)P_2(\cos\theta) + \dots , \quad (1)$$

where R is the distance between the H atom and the H_2 centre of mass, r is the H_2 bond length (assumed constant at $r_e = 1.4\,a_0$) and θ is the angle between $\boldsymbol{r}$ and $\boldsymbol{R}$.

Several empirical H–H_2 isotropic potentials encompassing the van der Waals minimum are available. In particular we cite those of Gengenbach et al. [9], Hishinuma [10], and Torello and Dondi [11]; Varandas [12] gives a comparison of several such potentials. The aim of this work is to determine whether any or all of these potentials support H_3 bound states.

All ground-state potential energy surfaces between uncharged species have a van der Waals minimum. However, if this minimum is shallow, there is no guarantee that it will support a bound state, especially for systems of light atoms which have large zero-point energies. It is believed, for example, that the minima in He–H_2 [13] and He–He [14] do not support any bound states, whereas the spectrum of H_2–H_2 is well characterised [15].

Within the Born–Oppenheimer approximation it is possible to solve the nuclear dynamics problem separately from the electronic problem. Here we do this for seven isotropic potentials [8–11] within the close-coupling formalism using the method of Le Roy and van Kranendonk [16]. This method has been successfully applied to several triatomics and in particular to H_2–inert-gas complexes. It has recently been reviewed by Le Roy and Carley [17]. Before turning to the nuclear dynamics, we will obtain an analytic estimate of the leading anisotropic term in the potential.

2. V_2 term

An expression for the anisotropic short-range repulsion energy was obtained by fitting the near Hartree–Fock SCF results of Varandas and Tennyson (ref. [8], column a in table 2) to a modified Born–Mayer potential

$$V_2^{\mathrm{HF}}(R) = A_2 \exp[-R(b_2^0 + b_2^1 R)] \tag{2}$$

in the range $3 \leqslant R \leqslant 9\, a_0$. Inside this range V_2 shows a complicated functional behaviour [12] associated with the singularity in the potential for linear geometries at $R = 0.7\, a_0$. This region of the surface is at high energy and need not concern us. A least-squares fit, weighted by $(V_2^{\mathrm{HF}})^{-1}$, gave $A_2 = 6.303$ cm^{-1}, $b_2^0 = 0.70275\, a_0^{-1}$ and $b_2 = 0.07342\, a_0^{-2}$. This fitted the calculated points with a typical 9% error.

The attractive long-range energy was assumed to take the form

$$V_2^{\mathrm{LR}}(R) = -\{1 - \exp[-R^2(d_1 + d_2 R^2)]\} C_6 \Gamma_6 R^{-6}, \tag{3}$$

where C_6 is the isotropic R^{-6} dispersion coefficient, taken after Meyer (quoted in ref. [11]) as 8.813 au. The term in braces damps the asymptotically correct multipolar expansion at short range to allow for overlap effects. Varandas and Tennyson's [8] values of $d_1 = -0.003625\, a_0^{-2}$ and $d_2 = 0.0012572\, a_0^{-4}$, obtained for their isotropic potential, were used.

For H–H$_2$, the ratio between anisotropic and isotropic dispersion terms, Γ_n, is only known for $n = 6$ [1]. The value of Γ_6 used, 0.11, is typical [1]. Although there is evidence from He–H$_2$ [13] that Γ_8 and Γ_{10} should be larger (of order 0.3), they are not known for H–H$_2$ and have been taken as zero.

The anisotropic potential

$$V_2(R) = V_2^{\mathrm{HF}}(R) + V_2^{\mathrm{LR}}(R) \tag{4}$$

has a shallow minimum of -0.7 cm^{-1} at $R \approx 6.5\, a_0$ and rises to +360 cm^{-1} at $R = 3.0\, a_0$ in excellent agreement with the anisotropic term obtained from integrating Varandas' LEPS potential [12].

As has been noted by Le Roy and van Kranendonk [16], anisotropic terms in the potential have little effect on the properties of H$_2$–X van der Waals molecules in their ground rotational state. This is because they only mix with the ground state through functions which represent rotationally excited states of H$_2$. These states are well spaced (typically 365 cm^{-1}) and the coupling is extremely small – it has often been ignored, for example in ref. [15]. In the case of H–H$_2$ the effect of V_2 is further reduced by the cancellation between the positive term at small R and the long, negative tail for large R when the potential is integrated over the range of the large-amplitude vibrations. The anisotropic term, however, still plays an important role in rotationally excited states and has thus been included in all the dynamical calculations presented in section 3.

3. Dynamical calculations

Any variational calculation, giving as it does only an upper bound to the energy, cannot rule out the existence of bound states on the evidence of an incomplete basis set calculation. To do this would require a method giving a lower energy bound. However, if variational calculations on a potential energy surface predict a bound state, then that surface does indeed support a bound state.

The variational method of Le Roy and van Kranendonk [16] was used to look for the H$_3$ bound states of the seven isotropic potentials listed in table 1. The method constructs a secular problem from basis functions, which can be represented by

$$[r^{-1}\phi_{vj}(r)]\,[R^{-1}\chi_{nl}(R)]\,\mathcal{Y}_{jl}^{JM}(\hat{R},\hat{r}), \tag{5}$$

where $\boldsymbol{R}$ and $\boldsymbol{r}$ are the vectors defined in section 1.

The first term in (5) represents the stretching motion of the H$_2$ diatom. As the diatom was considered as a rigid rotor with $r_e = 1.4\, a_0$ in its ground, $v = 0$, vibrational state, this term is unity in all basis functions.

The middle term in (5) represents the stretching vibrations of the H–H$_2$ complex. These radial basis functions were generated numerically for a pseudo-diatomic problem using the isotropic potential. In order to generate a complete basis it is necessary to include functions from the continuum and this is

Table 1
Energy of H_3 ($J = 0$) bound vibrational state for a selection of isotropic potentials, relative to H and p-H_2 at $R = \infty$. Also shown are van der Waals well depth (ϵ) and location (R_m), separation at zero energy (σ), and asymptotic coefficient of the R^{-6} dispersion term

Potential	Ref.	Energy (cm^{-1}) a)	ϵ (cm^{-1}) a)	R_m (a_0) a)	σ (a_0) a)	C_6 (au) a)
BMSV b)	[9]	−0.130	18.9	6.71	5.93	8.8
exp(11,6) c)	[10]	unbound	11.5	6.92	6.00	12.7
exp(12,6) c)	[10]	−0.039	14.4	6.65	5.84	5.46
exp(13,6) c)	[10]	−0.064	16.9	6.46	5.71	4.35
exp(14,6) c)	[10]	−0.091	19.4	6.33	5.63	3.68
MBMD d)	[11]	−0.116	14.8	6.56	5.66	8.813
MBMD d)	[8]	−0.163	17.0	6.58	5.73	8.813

a) 1 cm^{-1} = 1.9863×10^{-23} J molecule^{-1}, 1 a_0 = 0.52918 nm; 1 hartree a_0^{-6} = 9.573×10^{-36} J molecule^{-1} m^{-6}.
b) Three-region Born–Mayer–spline–van der Waals potential.
c) Modified Buckingham potential $\exp(\alpha, 6) = [\epsilon\alpha/(\alpha - 6)]\{(6/\alpha)\exp[\alpha(1 - R/R_m)] - (R_m/R)^6\}$.
d) Modified Born–Mayer–(damped) dispersion potential.

done by placing an infinite wall in the potential at a large value of R [18]. For the Varandas–Tennyson isotropic potential no bound states were obtained if this wall was placed closer than 30 a_0. At R_{wall} = 94.5 a_0, the isotropic potential, V_0, $\approx 2 \times 10^{-6}$ cm^{-1} and moving the wall was found to have little effect. This is indicative of the importance of the long attractive tail in stabilizing weakly bound states. All results presented here are for a wall in this position and a radial basis set of 5 functions, $n = 0, 1, 2, 3, 4$.

The angular basis set, $\mathcal{Y}_{jl}^{JM}$ in (5), is given in space fixed coordinates by

$$\mathcal{Y}_{jl}^{JM}(\hat{R},\hat{r}) = \sum_{m=-j}^{j} C(j,l,J;m,M-m,M) \times Y_{jm}(\hat{r})Y_{lM-m}(\hat{R}), \qquad (6)$$

where $C(j,l,J;m,M-m,M)$ is a Clebsch–Gordan coefficient. The quantum number j is associated with rotations of the H_2 diatom and l rotations (vibrations) of the vector $\boldsymbol{R}$. These couple to the total angular momentum J, which in the absence of nuclear hyperfine and electron spin interactions, is a good quantum number. For H_2, the nuclear symmetry means that only odd or even values of j can contribute to a particular state. Table 1 presents results for para-H_2 (j even) and $J = 0$. In all calculations, the angular basis set comprised of all functions with $j \leqslant 4$ which could couple to the relevant J state. Further details of the method are given by Le Roy and coworkers [16–18].

Table 1 shows that six of the seven potentials considered were found to support an H–H_2 bound state. The one exception being the $\alpha = 11$ potential of Hishinuma [10]. Although this potential gives a good representation of Hishinuma's data it has a well depth 20% less than any other potential considered and the whole potential is shifted to large R despite the the strongly over-attractive dispersion terms. Thus the short-range term for this potential is too repulsive. This illustrates a problem with inverting experimental data the characteristics of the potential can depend strongly on the form of the potential chosen. In Hishinuma's case, four equally good fits with slightly different model potentials give van der Waals well depths differing by nearly a factor of two.

Table 1 strongly implies the existence of an H_3 molecule even though nearly all the van der Waals well is taken up by zero-point energy. This results in a loosely bound, large-amplitude state. For example, the minimum of the Varandas–Tennyson [8] isotropic potential lies at 6.5 a_0, whereas the H–H_2 bound state has $\langle R \rangle = 16\, a_0$ and $\langle R^2 \rangle^{1/2} = 17\, a_0$ showing that this is indeed an extremely "floppy" state.

Next we investigated the effects of isotopic substitution and the differences between ortho and para diatomics. The results of these calculations, using the Varandas–Tennyson potential are given in table 2, which lists *all* the bound states found for the relevant species.

Table 2 shows that the general effect of isotopic substitution is to stabilize the van der Waals complex, as would be expected from the associated increase in

Table 2
Energy of bound X–Y_2 states for the isotropic potential of Varandas and Tennyson [8] relative to separated X + Y_2 species. o-H_2 is assumed to lie 121.9727 cm^{-1} above p-H_2 and p-D_2 60.9863 cm^{-1} above o-D_2

X	Y	Energy (cm^{-1})	J
H	p-H_2	−0.1632	0
H	o-H_2	−0.1632	1
D	p-H_2	−1.0744	0
D	o-H_2	−1.0744	1
H	o-D_2	−0.4909	0
H	p-D_2	−0.4909	1
D	o-D_2	−2.0373	0
		−0.8537	1
D	p-D_2	−2.0374	1
		−0.8541	2
		−0.8569	0

mass. This results in the stabilization of several rotational states for D_3. We found, however, no bound vibrationally excited states for any of the complexes examined.

For the lowest state of each complex, where the anisotropic potential has negligible effect, the vibrational wavefunction is completely dominated (greater than 99.99%) by the basis function which corresponds to the isotropic limit ground state. This means that these calculations are essentially converged by a basis set of only one function and results in there being little or no energy difference between ortho and para complexes, as hyperfine interactions have been ignored. For the rotationally excited states which are bound for D_3, the relevant isotropic unit basis function constitutes only ≈98% of the wavefunction. For these states the anisotropic potential is more important and thus the difference between ortho and para energies is an order of magnitude larger.

4. Conclusion

These calculations strongly imply the existence of at least one bound state for all the H_3 isotopic species. For H_3 an energy of -0.12 ± 0.05 cm^{-1} relative to dissociation is suggested by calculations on several potentials. This complex could well be formed in the low-density, low-temperature environment of space.

These calculations did not consider the hyperfine coupling between J and the diatomic nuclear spin. It is this coupling which has enabled H_2–H_2 to be observed [15] and could perhaps be the key to experimental observation of the ground-state H_3 molecule. In the case of D_3, several rotational states are found to be stable and it might be possible to observe its rotational spectrum. However, the anisotropic potential is important in calculating the stability of these states and the expression for V_2 given in section 2 can only be regarded as an estimate, lacking as it does, the higher dispersion terms.

Acknowledgement

The author would like to thank Professor Robert J. Le Roy for making available a copy of the programme written by him and J.E. Grabenstetter. He is also grateful to Professor Ad van der Avoird for helpful discussions of this problem and careful reading of the manuscript.

References

[1] D.G. Truhlar and R.E. Wyatt, Advan. Chem. Phys. 36 (1977) 141.
[2] D.G. Truhlar and R.E. Wyatt, Ann. Rev. Phys. Chem. 27 (1976) 1.
[3] G. Herzberg, J. Chem. Phys. 70 (1979) 4806.
[4] M. Jungen, J. Chem. Phys. 71 (1979) 3540.
[5] R.L. Martin, J. Chem. Phys. 71 (1979) 3541.
[6] B. Liu, J. Chem. Phys. 58 (1973) 1925.
[7] P. Siegbahn and B. Liu, J. Chem. Phys. 68 (1978) 2457.
[8] A.J.C. Varandas and J. Tennyson, Chem. Phys. Letters 77 (1981) 151.
[9] R. Gengenbach, Ch. Hahn and J.P. Toennies, J. Chem. Phys. 62 (1975) 3620.
[10] N. Hishinuma, J. Phys. Soc. Japan 41 (1976) 1733.
[11] F. Torello and M.G. Dondi, J. Chem. Phys. 70 (1979) 1564.
[12] A.J.C. Varandas, J. Chem. Phys. 70 (1979) 3786.
[13] W. Meyer, P.C. Hariharan and W. Kutzelnigg, J. Chem. Phys. 73 (1980) 1880.
[14] H.G. Bennewitz, H. Busse, H.D. Dohmann, D.E. Oates and W. Schrader, Z. Physik 253 (1972) 435.
[15] J.F.C. Verberne and J. Reuss, Chem. Phys. 50 (1980) 137; 54 (1981) 189.
[16] R.J. Le Roy and J. van Kranendonk, J. Chem. Phys. 61 (1974) 4750.
[17] R.J. Le Roy and J.S. Carley, Advan. Chem. Phys. 42 (1980) 353.
[18] R.J. Le Roy, J.S. Carley and J.E. Grabenstetter, Faraday Discussions Chem. Soc. 62 (1977) 169.