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Rovibrational spectrum of the excited potential energy surface of $He+H_2$ ($B\ ^1\Sigma_u^+$)

Stavros C. Farantos[a)]
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., Athens 116/35, Greece

Jonathan Tennyson
Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England

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Recently MRD-CI calculations on the He + H_2 × ($B\ ^1\Sigma_u^+$) potential surface have revealed the existence of a minimum of 1.5 eV in contrast to the very shallow van der Walls minimum in ground state He + H_2 × ($X\ ^1\Sigma_g^+$).[1] In the region of the minimum there is a strong interaction with the ground state and the two surfaces approach each other. These findings have led to a qualitative explanation of the strong electronic quenching of the HD($B\ ^1\Sigma_u^+$) state in collisions with He observed by Fink *et al.*[2]

Using *ab initio* calculations Farantos *et al.*[3] have produced analytical potential energy functions for the ground and the first singlet excited state of HeH_2. The functions describe all nuclear configuration space and obey the symmetry of the system.

The excited surface has the minimum located at the geometry $R_{HeH_1} = 3.57a_0$, $R_{HeH_2} = 1.47a_0$ and the angle between them 103°. The symmetric minima are separated by a barrier of about 72 000 cm^{-1}, whereas the barriers to linear structures H–He–H and H–H–He are 7300 and 13 700 cm^{-1}, respectively. This potential has been used in quasiclassical trajectory calculations of the collisions of He with $H_2(B\ ^1\Sigma_u^+)$.[4]

To our knowledge there are no first principles rovibrational calculations on an electronically excited state of a polyatomic system. Excited states present new challenges for vibrational computations because some exotic topological features may occur. Thus HeH_2 provides an opportunity to carry out such a study. Moreover the assignment of the spectroscopic features of the $HeH_2(A\ ^1A')$ state may prove useful for analysing experiments on this system.

The calculations were performed with the method of Tennyson and Sutcliffe,[5] using program ATOMDIAT[6] with the extension GENPOT[7] to allow for a generalized potential. This method has been successfully applied to the rovibrational problem for a variety of triatomics. These range from van der Waals molecules H_2Ne[5] and HFHe,[5] through the floppy KCN[5] and CH_2^+[8] systems, to more conventional molecules (with small amplitude vibrational modes) such as H_3^+ and H_2D^+,[9] and H_2F^+ and H_2Cl^+.[10] Molecules with more than one potential minimum, such as LiCN,[11] have also been successfully treated. Indeed, this method which makes no *a priori* assumptions about equilibrium structure, should be particularly suitable for systems such as $HeH_2(A\ ^1A')$ which have multiple minima.

In this paper we present computations for the $J = 0$ and 1 levels of $HeH_2(A\ ^1A')$. Test calculations were performed with both Morse oscillator-like[5,6] and spherical oscillator-like[7,8] basis functions for the He–H_2 stretching coordinate. As has been observed previously,[9] the Morse-like functions proved more efficient for this nonlinear system.

For the $J = 0$ states of HeH_2 we used up to 612 basis functions—6 in each stretching coordinate and 17 Legendre functions for each symmetry. That allowed us to obtain the first 10 levels converged to about 1 cm^{-1};

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TABLE I. Vibrational levels (in cm^{-1}) of $HeH_2(A\ ^1A')$. Ground state energies are given relative to the minimum $-12\,756\ cm^{-1}$. $J = 1$ levels relative to HeH_2 (0, 0, 0) are also shown.

(v_1, v_2, v_3)	Even	Odd
(0, 0, 0)	−9394.4	−9394.4
(0, 1, 0)	1161.9	1161.9
(0, 0, 1)	1438.2	1438.2
(0, 2, 0)	2291.6	2291.5
(0, 1, 1)	2575.2	2575.2
(0, 0, 2)	2813.7	2813.6
(0, 3, 0)	3410.1	3409.9
(0, 2, 1)	3699.6	3699.7
(1, 0, 0)	3868.6	3868.3
(0, 1, 2)	3922.5	3922.6
	$J = 1$	
−1	10.09	10.09
0	43.72	43.71
1	44.46	44.43

the results are given in Table I. For the r coordinate, H–H stretch, optimized parameters[6] for the Morse oscillator were found to be $r_e = 4.245a_0$, $D_e = 0.40E_h$, and $\omega_e = 0.0070E_h$. For the R coordinate, He–H_2 stretch, the parameters were $R_e = 2.00a_0$, $D_e = 0.02E_h$, and $\omega_e = 0.040E_h$.

In HeH_2, the two minima, symmetric with respect to the C_{2v} axis give nearly degenerate vibrational levels which are either even or odd under interchange of two H atoms. The high barrier meant that any splitting was less than the accuracy of our calculation and any tunneling was negligible for the low-lying vibrational states.

The fundamentals $\omega_1 = 3868.6\ cm^{-1}$, $\omega_2 = 1161.9\ cm^{-1}$, and $\omega_3 = 1438.2\ cm^{-1}$ correspond to the short HeH stretch, to the bend, and long HeH stretch, respectively. The large value of ω_1 is a reflection of the strength of the short HeH bond. ω_1 is also increased by resonance interaction with the $2\omega_2 + \omega_3$ mode. This combined with anharmonic effects gives a zero point energy for HeH_2 which is $125\ cm^{-1}$ above the harmonic value of 1/2 $(\omega_1 + \omega_2 + \omega_3)$.

From the rotationally excited state we computed the rotational constants $A_0 = 39.04$, $B_0 = 5.42$, and $C_0 = 4.71\ cm^{-1}$; the molecule is a nearly prolate symmetric top ($k = 0.96$).

We hope that the above spectroscopic constants will aid the experimental observation of this species.

[a] Permanent address: Department of Chemistry, University of Crete, Iraklion, Crete, Greece.

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Kinetic energy dependence of ion-polar molecule collision rate constants by trajectory calculations

Timothy Su
Department of Chemistry, Southeastern Massachusetts University, North Dartmouth, Massachusetts 02747

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In recent years, much experimental work has been performed to examine the kinetic energy dependence of ion–molecule reactions.[1] In this work, while the ion–molecule relative kinetic energy is varied from near thermal energies to a few eV, the rotational energy of the reactant neutral remains at a specified temperature. Consequently, there is a growing need for a collision theory that describes the kinetic energy dependence of rate constants when the neutral remains at a given temperature. Thermal capture rate constants for ion–polar molecule collisions have been calculated recently using the trajectory method.[2,3] In that study, the ion was treated as a point charge and the polar molecule as a two-dimensional rigid rotor. The interaction potential was assumed to have the form

$$V(r, \theta) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2}\cos\theta, \tag{1}$$

where α and μ_D are the (angle-average) polarizability and dipole moment of the neutral, r is the distance between the ion and the center of mass of the neutral, θ is the

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