Rovibrational spectrum of the excited potential energy surface of He+H2 (B 1#u+)

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Rovibrational spectrum of the excited potential energy surface of He+H$_2$ ($B\ ^1\Sigma_u^+$)

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Recently MRD-CI calculations on the He + H$_2$ $\times$ ($B\ ^1\Sigma_u^+$) 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$_2$ $\times$ ($X\ ^1\Sigma_g^+$).[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 $R_{\mathrm{HeH_1}} = 3.57a_0$, $R_{\mathrm{HeH_2}} = 1.47a_0$ 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$_2$Ne[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$_2$D$^+$,[9] and H$_2$F$^+$ and H$_2$Cl$^+$.[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.

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

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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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