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Predicted vibration–rotation levels of H_2He^+ and its isotopomers

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Variational bound state nuclear motion calculations are performed on a fitted [Joseph and Sathyamurthy, J. Chem. Phys. **86**, 704 (1987)] *ab initio* surface for HeH_2^+. The linear $^4HeH_2^+$ molecule is predicted to have an He–H_2^+ stretch fundamental of 732 cm^{-1} with the first $J = 0$ excited bend at 960 cm^{-1}. This isotopomer has no bound excited states of the H_2^+ vibrational mode. Calculations with $J = 1$ and $J = 2$ predict a rotational constant of 4.0 cm^{-1} for this system. Results are also presented for all the isotopomers containing D and ^3He. The spectrum of this molecule is a good candidate for laboratory or astrophysical observation.

I. INTRODUCTION

Simple molecular systems containing helium and hydrogen have proved to be of considerable interest to both experimental and theoretical chemists for the past two decades, since the photoionization experiments of Chupka and co-workers on HeH^+.[1] Any molecule containing these two most abundant elements is also likely to be of astronomical importance. HeH^+ itself features prominently in the work of Black,[2] Roberge and Dalgarno,[3] and Flower and Roueff.[4]

Recently, Joseph and Sathyamurthy[5] (JS) published theoretical calculations on the formation of HeH^+. The basis of these calculations was the accurate *ab initio* CI data of McLaughlin and Thompson[6] (MT) for the system He–H_2^+. The MT calculations recovered 90% of the correlation energy of the system. JS used a Murrell–Sorbie[7] potential to represent a grid of 526 points. With this surface they achieved near-quantitative agreement between their calculations and Chupka's experimental results[1] for the reaction

$$He + H_2^+ \rightarrow HeH^+ + H. \tag{1}$$

This reaction has an analogous place in the interstellar chemistry of He to the reaction of $H_2 + H_2^+$, yielding the widely studied[8] H_3^+ ion, in that of hydrogen. It is therefore of considerable importance.

What is also of interest, however, is that the MT calculations and the surface of JS predicts that the triatomic ion HeH_2^+ will be stable with respect to all dissociation products. The shallow, symmetry-related minima are 0.25 eV below the lowest dissociation limit of He + H_2^+ and have a linear geometry with the H–H and the short H–He separations both near 2 a_0. This means that the triatomic ion is over 1 eV more stable than HeH^+ and that it can have a number of rotational and vibrational bound states. Thus there is the possibility of predicting rotation–vibration energy levels from which infrared and microwave spectra could be deduced.

Previous experimental work[9] and theoretical considerations[10] indicate that HeH_2^+ has already been prepared in the laboratory. Astrophysically, the molecule may also be a candidate for observation since, once formed,[2,9] its rate of destruction should be some 10^{-4} times slower than that of HeH^+.

The object of this current work is to calculate the rovibrational energy levels of $^4HeH_2^+$ and its ^3He and deuterated isotopomers using the surface of JS. It is hoped that the levels calculated may be of assistance in the detection of HeH_2^+ both in the laboratory and in favorable regions of interstellar gas clouds. It is also hoped that the isotope effects reported below may prove a useful handle for astrochemists trying to ascertain the all-important ^3He:^4He ratio.

II. METHOD

The calculations presented here were all performed using the variational method developed by Tennyson and Sutcliffe (TS)[11–13] for treating triatomic systems with one or more large amplitude vibrational modes. For the symmetric isotopomers, i.e., those containing H_2 or D_2, the calculations employed scattering coordinates. These coordinates are the H–H (D–D) separation r; the distance of He to the H_2 (D_2) center of mass R, and the angle θ between $\mathbf{r}$ and $\mathbf{R}$. For complexes involving HD a similar coordinate system was used in which R and θ were defined from the geometric center of the HD bond.

For a discussion of the merits of and the explicit form of the Hamiltonian for both these coordinate systems, see Ref. 11. We will only comment that the geometric coordinates used for the $HeHD^+$ complexes retain the symmetry of the potential but introduce asymmetric terms via the kinetic energy operator. This feature proved vital when calculations were performed on the complex formed by HD($B\,^1\Sigma^+$) and He,[11,14] a nonrigid system which has two symmetry-related minima in its potential.

The HeH_2^+ molecule is particularly suited to the approach of TS as it is naturally represented as a scattering complex between H_2^+ and He. This is demonstrated by the low frequency of the vibrational modes involving He and the small shifts in the HD^+ and D_2^+ vibrational modes upon complex formation. The method used allows vibrational states localized in either of the linear minima to be represented simultaneously and thus accounts correctly for any interaction (tunneling splitting) between them. Furthermore, the linear equilibrium structure means that the projection k of the total angular momentum J along the molecular axis is very nearly a good quantum number. Indeed, if it were not for the bending modes, this would be rigorously so. This means that the system lends itself well to the two-step variational procedure of Tennyson and Sutcliffe[12] which solves the full rotational problem using basis functions generated, assuming k to be a good quantum number.

As in previous calculations on floppy systems,[13] the basis functions were written as a product of one-dimensional functions adapted to each coordinate. Associated Legendre functions $\theta_{j,k}(\theta)$ were used to represent motions in the angular coordinate, with k fixed as discussed above. In these functions, j represents the rotations of the diatomic—in this case H_2^+. The radial coordinates were represented by Morse oscillator-like functions[15] for which the usual Morse parameters (r_e, D_e, ω_e) were optimized for each coordinate.

Because the H_2He^+ molecule behaves like an H_2^+–He collision complex, we were able to optimize basis functions separately for the two radial coordinates. Those for the r coordinate were chosen to give a good representation of the relevant diatomic, see Table I; those for the R coordinate were optimized for the atom–rigid diatom system obtained by freezing r at the equilibrium separation of 2.0 a_0. Initially, a basis set was developed for $H_2{}^4He^+$. It was found that the optimum value of ω_e for the r coordinate changed with deuteration, but that the R and other r coordinate parameters in the basis functions were insensitive to isotopic substitution. For the R coordinate basis set parameters $R_e = 3.47\ a_0$, $D_e = 0.015\ E_h$, and $\omega_e = 0.0025\ E_h$ were used in all calculations.

All calculations reported here were performed with programs TRIATOM and ROTLEV.[18] We note that recent calculations by us on H_3^+ using these programs and the method described here obtained almost exact agreement with experiment.[19]

$J = 0$ calculations were performed on H_2He^+ and D_2He^+ using all five functions with $m \leqslant 4$ in the r coordinate, all nine with $n \leqslant 8$ in the R coordinate and angular functions with $j \leqslant 13$. This gave two secular problems, one for para-H_2^+ (j even) and one for ortho-H_2^+ (j odd), each of dimension 315. The $HDHe^+$ calculations used basis sets of the same size, but of course the lowering of symmetry leads to a single secular problem of twice the size. Test calculations suggested that this was sufficient to calculate the fundamental frequencies to better than 0.1 cm^{-1} and higher levels to only slightly worse than this. This level of accuracy is probably better than warranted by the JS surface.

Calculations on rotationally excited states were performed with the molecular z axis placed along both **r** and **R**. Both embeddings gave a good representation of the system. The best being for the **R** embedding for which only the 20 lowest solutions of the vibrational problem for each k were needed to converge the fully Coriolis coupled problem.[12] This gives a modest basis—the largest secular problem reported here is thus only 60 dimensional ($J = 2$ even parity calculations)—sufficient to converge the rotational part of the calculation to very high accuracy. As k is very nearly a good quantum number for this system (all $J = 1$ levels reported below was at least 99% one pure k level) k has been used to label the states presented below. We note that if the molecules were rigidly linear $|k|$ would be identical to $|l|$, the quantum number conventionally used for the projection of angular momentum along the axis of a linear molecule.

In labeling the results, we have used assignments adopted for linear molecules.[20] Thus states with parity $(-1)^{J+p}$ have been labeled $e(p = 0)$ or $f(p = 1)$, and only states with even quanta of the bending mode are found for $J = 0$.

III. RESULTS AND DISCUSSION

Table I compares calculations on the H_2^+ diatomic species with effectively exact calculations on the same systems. As the optimized Morse oscillator-like basis functions converged all the levels to within 0.2 cm^{-1}, the differences between the results can be attributed to errors in the JS potential.

Tables II–V give the results of our calculations on the HeH_2^+ complexes. The absolute binding energies given in Tables II–IV are given relative to the dissociation products of atomic He and the appropriate H_2^+ isotopomer. In calculating this energy, allowance has been made for the zero-point energy of the ion in question. For symmetric complexes with j odd the H_2^+ (D_2^+) dissociation product cannot occupy a $J = 0$ state. The additional energy of dissociating

TABLE I. Comparison of zero-point energies and $J = 0$ vibrational levels of H_2^+, HD^+, and D_2^+. (i) Calculated using the extended Rydberg potential of JS (Ref. 5) and a basis of five Morse oscillator-like functions (Ref. 15) with parameters (r_e, D_e, ω_e). (ii) Calculated by direct numerical integration (Ref. 16) of the exact potential (Ref. 17).

	H_2^+		HD^+		D_2^+	
	JS	Exact	JS	Exact	JS	Exact
zpe[a]/cm^{-1}	− 21 308.8	− 21 375.9	− 21 463.3	− 21 528.7	− 21 647.2	− 21 709.9
$v = 1/cm^{-1}$	2 216.9	2 192.1	1 936.2	1 913.2	1 597.1	1 577.4
$v = 2/cm^{-1}$	4 301.5	4 256.9	3 772.2	3 730.3	3 125.9	3 090.1
r_e/a_0	2.2		2.2		2.2	
D_e/E_h[b]	0.05		0.05		0.05	
ω_e/E_h[b]	0.0090		0.0075		0.0060	

[a] Zero-point energy relative to dissociation.
[b] $1\ E_h = 219\ 474.6\ cm^{-1}$.

TABLE II. Calculated rovibrational levels of $^4HeH_2^+$ in cm^{-1}. The frequencies of the $J = 0$ levels are given relative to the ground state, which in turn is given relative to the $HeH^+ + H$ dissociation limit. The rotationally excited levels are given relative to the corresponding $J = 0$ vibrational level. The complexes dissociating to para-H_2^+ (j even) and ortho-H_2^+ (j odd) are considered separately. The vibrational states are labeled by their degree of He–H_2 bending ν_b, and stretching ν_s, excitation. All levels are for the H_2^+ mode in its $v = 0$ state.

	$E(0,v_b,v_s) - E(0,0,0)$	$E(0,v_b,v_s,J,k) - E(0,v_b,v_s,0,0)$							
ν_b ν_s	$J = 0$	$J = 1^e$		$J = 1^f$	$J = 2^e$			$J = 2^f$	
		$k = 0$	$k = 1$	$k = 1$	$k = 0$	$k = 1$	$k = 2$	$k = 1$	$k = 2$
j even									
0 0	(− 1792.80)	8.02	472.1	472.4	24.04	488.1	988.7	488.7	988.1
0 1	732.0	7.40	430.5	430.7	22.20	445.0	885.8	445.8	885.8
2 0	959.9	7.97	467.9	468.9	23.84	482.1		484.8	
0 2	1330.6	6.65	387.1	387.5	19.95	399.8		402.1	
2 1[a]	1581.0	7.68			22.98				
4 0[a]	1785.1								
j odd									
0 0	(− 1792.80)	8.02	472.1	472.3	24.04	488.1	989.1	488.7	988.5
0 1	732.0	7.40	430.2	430.4	22.20	444.8	890.0	445.4	890.1
2 0	960.7	7.90	459.8	459.9	23.62	476.0		476.4	
0 2	1330.7	6.65	385.8	386.1	19.95	398.8		400.6	
2 1	1589.7	6.89			20.59				
4 0[a]	1801.2	6.26							

[a] These assignments are approximate as the states show some delocalization.

into a $J = 1$ state has not been explicitly included, as this would obscure the near degeneracy between j odd and j even levels, but has been used when determining which states of the complex are bound.

Table II presents results of calculations on $^4HeH_2^+$. The table gives all the bound states of the complex which we found with total angular momentum less than or equal to 2. We did not make a serious attempt to identify further high-lying, possibly diffuse, bound states as these probably have little spectroscopic significance. The results in Tables II and III are divided between those which dissociate into ortho-H_2^+ (D_2^+) and those which dissociate into para-H_2^+ (D_2^+). Because of the symmetry related double minima in the potential, the difference between these states is whether their wave functions are symmetric (j even) or antisymmetric (j odd) about $\theta = 90°$. An example is shown in Fig. 1. Vibrational assignments were made by plotting contours of the wave functions and analyzing the nodal structure of the wave function in the region $\theta < 90°$. These assignments were easily made but in certain cases, as indicated, must be regarded as approximate because of delocalization across the barrier separating the two minima, see Fig. 2.

TABLE III. Zero-point energies and vibrational band origins, $E(v_r,v_b,v_s) - E(0,0,0)$, of the symmetric isotopomers of HeH_2^+, in cm^{-1}. The levels are labeled according to the degree of excitation of H_2^+ ν_r, the He–H_2^+ bending mode ν_b, and the He–H_2^+ stretching mode ν_s.

	j even			j odd		
$\nu_r\nu_b\nu_s$	$^3HeH_2^+$	$^4HeD_2^+$	$^3HeD_2^+$	$^3HeH_2^+$	$^4HeD_2^+$	$^3HeD_2^+$
0 0 0	− 1767.41	− 1953.28	− 1921.91	− 1767.41	− 1953.28	1921.92
0 0 1	763.3	609.5	645.5	763.3	609.5	645.5
0 2 0	965.3	690.5	704.4	966.2	698.9	704.4
0 0 2	1376.7	1141.6	1207.1	1376.9	1141.6	1207.1
0 2 1	1606.5[a]	1252.4	1297.1	1618.4	1252.2	1297.0
0 4 0		1362.0	1378.3		1362.1	1378.7
1 0 0		1420.2	1424.2		1420.2	1424.2
0 0 3		1591.0	1669.7		1591.0	1669.7
0 2 2		1728.7	1791.4		1728.7	1791.8
0 4 1		1829.3[a]	1854.2[a]		1844.9[a]	1879.2[a]

[a] These assignments are approximate as the states show some delocalization.

TABLE IV. Zero-point energies and vibrational band origins, $E(v_r,v_b,v_s) - E(0,0,0)$, of the asymmetric isotopomers of HeH_2^+, in cm^{-1}. The levels are labeled according to the degree of excitation of HD^+ ν_r, the He–HD^+ bending mode ν_b, and the He–HD^+ stretching mode ν_s.

$\nu_r\nu_b\nu_s$	$^4HeDH^+$	$^4HeHD^+$	$^3HeDH^+$	$^3HeHD^+$
0 0 0	− 1917.35	− 1838.68	− 1888.04	− 1810.61
0 0 1	660.4	641.7	697.5	677.5
0 2 0	761.3	907.1	769.8	914.6
0 0 2	1218.7	1199.1	1277.6	1256.6
0 2 1	1334.0	1255.3	1368.4	1508.0
0 4 0	1559.7	1697.7[a]	1578.2	1683.9[a]
1 0 0	1708.4	1749.0[b]	1712.5	1701.7
0 0 3	1672.6	1651.1[b]	1739.8	1768.7
0 2 2	1816.7[a]		1863.1[a]	

[a] Because of delocalization, the assignment of these states to a specific isomer and vibrational levels is only approximate.

[b] These states are strongly coupled.

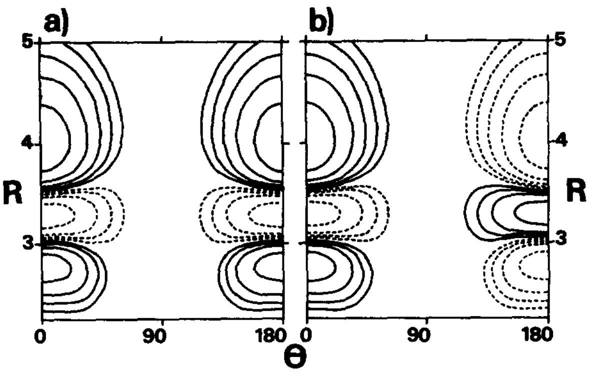

FIG. 1. Wave functions of the $^4HeH_2^+$ vibrational state (0,0,2) with (a) j even and (b) j odd. The plot is for H_2^+ frozen at $r = 2.0\ a_0$. Contours link points 64%, 32%, 16%, 8%, and 4% of the maximum amplitude of the wave function. Solid (broken) curves enclose regions of positive (negative) amplitude. The vertical scale is R, the distance between He and the center of mass of the diatomic, in atomic units. The horizontal scale is θ, the angle between R and the diatomic bond r in degrees.

The splitting of the rovibrational levels in the symmetric isotopomers is very small for the low-lying levels which are probably the most important spectroscopically. This suggests that there is little tunneling in this region and that complex can be thought of approximately as one in which the He is localized at one end of the complex. For this reason the distinction between j even and j odd complexes has been dropped in Table V.

Localization is indeed observed in the plots of the wave function for the complexes involving HD^+, see Fig. 3. For this reason, all $HeHD^+$ results shown in Tables IV and V have been classified according to whether the He is near the D or H. $HeDH^+$ is the more stable isomer. There are considerable changes in the frequencies of the complex modes between different $HeHD^+$ isomers/isotopomers. This is reflected in Table IV where the ordering of assignments inevitably leads to some levels appearing not in energy order.

Because the binding energy of the complexes is similar in magnitude to the fundamental frequency of H_2^+, it is interesting to note that this mode is only observed in complexes containing D. In these complexes, the fundamental frequency appears to have been shifted to about 90% of the free ion values given in Table I. The variation in frequency between complexes of the same hydrogen ion can be explained by the presence of Fermi resonances with overtones of the complex. These manifest themselves as distortions of the wave function on our contour plots. The coupling is particularly strong between the (0,0,3) and (1,0,0) modes of $^4HeHD^+$, which would otherwise be very close in energy.

HeH_2^+ has a linear geometry at the potential minima. If the molecule was rigidly linear then k (or l) would be a good quantum number and states with the same k but differing in parity would be degenerate. As can be seen from Tables II and IV, a consideration of the full nonrigid problem shows that this degeneracy is only weakly lifted by the bending motion, i.e., l doubling is small. For a linear molecule the k or l equals 1 levels correspond to one bending of vibrational excitation. In all cases considered here the ground state to lowest $\nu_b = 1^1$ level is less than half that of going to the $\nu_b = 2^0$ state.

Finally, we note that the $J = 2$, $k = 2(\nu_b = 2^2)$ degeneracy of the ground state of $^4HeH_2^+$ is broken by the proximity of the $J = 2$, $k = 0$ state with $\nu_b = 2^0$ in the e parity block. However, even for these states, the wave function is more than 95% composed of the k value under which the states are classified.

TABLE V. Lowest $J = 1$ rotational levels in cm^{-1} relative to the lowest $J = 0$ vibrational level of the isotopomers of HeH_2^+, $E(0,0,0,J,k) - E(0,0,0,0,0)$.

	$J = 1^e$		$J = 1^f$
	$k = 0$	$k = 1$	$k = 1$
$^4HeH_2^+$	8.02	472.1	472.4
$^3HeH_2^+$	8.75	475.3	475.5
$^4HeD_2^+$	5.14	324.8	325.0
$^3HeD_2^+$	5.81	329.6	329.8
$^4HeDH^+$	7.57	364.1	364.3
$^4HeHD^+$	5.20	440.2	440.3
$^3HeDH^+$	8.42	368.5	368.7
$^3HeHD^+$	5.84	443.5	443.6

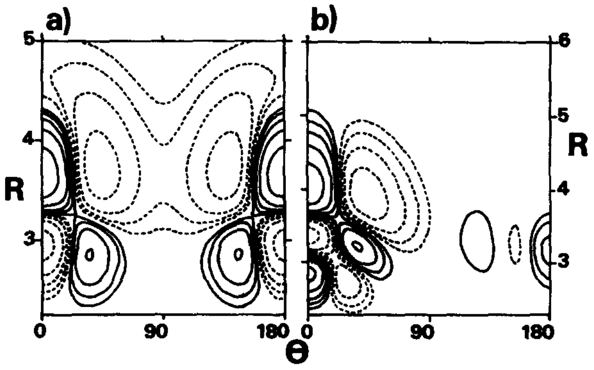

FIG. 2. Wave functions of the delocalized vibrational states (a) (0,2,1) j even of $^4HeH_2^+$ and (b) (0,2,2) of $^4HeDH^+$. Details as for Fig. 1.

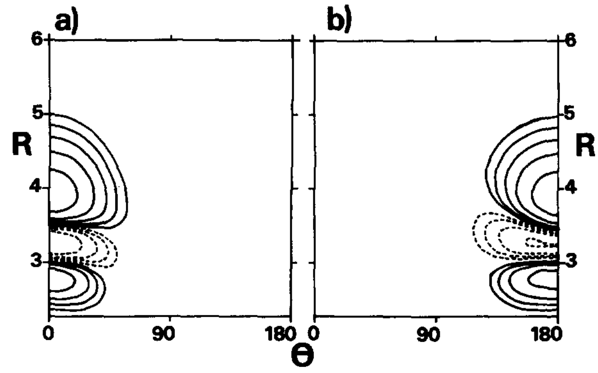

FIG. 3. Wave functions of the vibrational state (0,0,2) for (a) $^4HeDH^+$ and (b) $^4HeHD^+$. Details as for Fig. 1.

IV. CONCLUSIONS

We have performed rovibrational calculations to determine the bound states of a recently proposed surface of the HeH_2^+ molecule. We hope that the predicted levels will be useful to spectroscopers or astronomers searching for the as yet unobserved spectrum of this species.

When considering the accuracy of the calculations such as those presented here, it is not only necessary to consider the accuracy of the rovibrational calculations, which is undoubtedly very high,[19] but also any errors in the underlying potential. McLaughlin and Thompson[6] claimed that their CI calculations accounted for 90% of the correlation energy in the complex. This should be sufficient to give good, probably accurate to about 1%, estimates of the vibrational fundamentals of the system. As the comparison in Table I shows, this is the level of accuracy achieved for isolated hydrogenic systems H_2^+, D_2^+, and HD^+.

However, there is a problem with the analytic representation of the potential over a wide region of the coordinate space. The fit of Joseph and Sathyamurthy[5] to the *ab initio* data has a standard deviation of 600 cm^{-1}. This figure is dominated by points well above the dissociation limit of the complex which are of little significance to its spectroscopy. However, it does seem likely that the fitting of the surface is a major source of error in the current calculations.

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