CALCULATION OF THE HIGH ANGULAR MOMENTUM DISSOCIATION LIMIT FOR H_3^+ AND H_2D^+

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Ab initio rotation–vibration calculations are presented for four H_3^+ potential energy surfaces with a view to determining a variational lower bound on the highest angular momentum state of H_3^+ and H_2D^+ supported by each potential. The calculations are performed using a two-step variational method and retain all ro-vibrational couplings. The results are found to be insensitive to the details of the potential other than the dissociation energy. For each of the three most accurate potentials $J=46$ and $J=54$ are the highest states found for H_3^+ and H_2D^+ respectively.

The spectroscopy of H_3^+ and its isotopomers has been the subject of considerable study in the 1980s [1]. In particular the still unassigned near-dissociation spectra recorded by Carrington and Kennedy [2,3] has given rise to much interest and speculation. The generally accepted explanation of these extremely rich spectra is that high angular momentum states are being observed with the final state undergoing rotational predissociation [4–7]. However, there is still little experience on how strongly bound systems behave near such a rotationally induced dissociation limit. The purpose of this Letter is to report near-dissociation calculations performed on four potentials [8–11] all of which have been used for dynamical calculations on the H_3^+ system. These calculations were performed to determine the highest truly bound angular momentum state supported by each of the potentials.

Three of the potentials, those due to Schinke, Dupuis and Lester (SDL) [9], Martire and Burton (MarB) [10] and Meyer, Botschwina and Burton (MBB) [11], are fits to high accuracy ab initio electronic structure calculations. The most accurate of these, due to MBB, reproduces the known spectrum of H_3^+ and its isotopomers to within 0.1% [12]. The fourth potential is a diatoms-in-molecules (DIM) potential [8] which has been used extensively for (semi)-classical calculations [6,13]. An important difference between the potentials is that while the SDL and DIM potentials correctly reproduce the lowest dissociation limit of H_3^+ to H_2+H^+, the MarB and MBB potentials do not. These latter potentials are expressed as displacements from the H_3^+ equilibrium structure and are not valid for excitation energies as low as half way to dissociation.

The calculations were performed using the two-step variational procedure of Tennyson and Sutcliffe [14]. The first variational step involves solving a series of vibrational problems in which it is assumed that k, the projection of the total angular momentum, J, along the body-fixed z axis is a good quantum number. In the second step enough solutions of the first step are used to ensure convergence. All the calculations presented here used a modified [15] version of the programs SELECT, TRIATOM and ROTLEV [16] and a scattering coordinate system.

The basis sets employed were products of rotation matrices, associated Legendre functions for the bending coordinate and Morse-oscillator-like functions [17] for the two radial coordinates: the H–H stretch, r_1, and the H–H_2 stretch, r_2. As discussed below, the Morse potential parameters which define these functions, r_e, D_e and ω_e, can be optimised to give the best basis set for a particular calculation [16].

Basis functions for both first and second steps of the calculations were chosen by energy ordering [15,16]. The N_{sel} basis functions with the lowest di-

Table 1
Optimised parameters used in the Morse-oscillator-like functions [17]

	H_3^+				H_2D^+			
	$J=46$		$J=0$ [18]		$J=54$		$J=0$ [18]	
	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
r_e (a_0)	2.40	3.40	1.71	1.68	2.00	3.42	1.71	1.65
D_e (E_h)	0.050	0.130	0.100	0.260	0.050	0.160	0.100	0.215
ω_e (E_h)	0.0069	0.0064	0.0118	0.0110	0.0090	0.0044	0.0118	0.00895

agonal matrix elements were chosen from a $k=0$ calculation in SELECT for the first step, no Coriolis calculations performed by TRIATOM. From the $N_{sel}(J+1)$ solutions of these calculations with $k=0$-J, the N_{bas} functions with the lowest eigenenergies were chosen for the second step performed by ROTLEV. This selection had the constraint that not more than N_k^{max} functions were chosen for a particular k.

In order to obtain converged results it is necessary to consider the behaviour of both steps in the calculations with respect to increasing the basis sets. It was soon apparent that the vibrational basis sets developed previously [18] for calculations with low values of J gave a poor representation of the highly rotationally excited, near dissociation states under consideration here. The H_3^+ parameters were therefore reoptimised for a $J=46$ calculation for which $k=0$ was assumed. Similarly the H_2D^+ parameters were optimised for $J=54$. Table 1 gives the details.

One would expect that the centrifugal distortion of the molecules would lead to a general increase in their size. This is reflected in the parameters used for the Morse-oscillator-like functions used to represent the stretching coordinates. It was also reflected in the enlarged region of the potential sampled by our numerical integration procedure. This meant that extra care was required in removing the effects of regions of the potential for which the analytic forms were no longer valid.

Tables 2 and 3 illustrate the convergence of both variational steps for calculations on H_3^+ using the MBB potential. As the effect of increasing J by one is to raise the energy of the lowest state in H_3^+ by about 800 cm^{-1} and H_2D^+ by about 650 cm^{-1}, convergence to about 1 cm^{-1} was considered more than sufficient for our current purpose. Actually the higher J levels involved in the H_2D^+ system meant that convergence very much better than this was actually achieved for this system.

In order to determine the highest bound state of each potential it is necessary to have an estimate of the dissociation energy, E_D, for each potential. The lowest dissociation limit for H_3^+ is to $H_2(v=0)+H^+$ and for H_2D^+ to $HD(v=0)+H^+$. It is therefore necessary to allow for both the electronic and the vibrational zero-point components of the dissociation energy for each potential. For the ab initio potentials the electronic dissociation energy, E_D^{elec}, was obtained by considering the energy difference between

Table 2
Convergence of $J=46$, $k=0$ H_3^+ calculations on the MBB potential as a function of the number of basis functions included in the basis. Wavenumbers, in cm^{-1}, are relative to dissociation into $H+H+H^+$

N_{sel}	$J=46$ optimised [a]		$J=0$ optimised [a]	
	level 1	level 10	level 1	level 10
600	−32295.0	−29562.8	−27753.7	−22132.5
800	−32295.0	−29571.5	−27753.7	−22132.5
1000	−32995.0	−29571.7		

[a] See table 1.

Table 3
Convergence of full $J=46$ H_3^+ calculations on the MBB potential as a function of the number of basis functions included in the basis. Wavenumbers, in cm^{-1}, are relative to dissociation into $H+H+H^+$

N_{sel}	N_k^{max}	N_{bas}	Level 1	Level 2
800	600	5000	−36487.7	−36278.3
800	600	6000	−36489.9	−36298.8
800	600	7000	−36492.8	−36314.5
800	600	8000	−36495.5	−36324.6
800	600	9000	−36496.7	−36332.7
800	600	9500	−36496.8	−36333.7
1000	600	8000	−36494.6	−36319.0
1000	700	8000	−36495.9	−36319.3
1000	700	9000	−36496.9	−36331.2

the H_3^+ minimum and the H_2 minimum calculated with the same basis. The vibrational contribution was estimated from solutions of the effectively exact H_2 potential [19] as 2179.7 cm^{-1} for H_2 and 1971.7 cm^{-1} for HD.

Table 4 gives details of the dissociation energy calculated for each potential and the lowest level, $E_J(1)$, for highest truly bound and lowest unbound J state. The results in table 4 are only for the totally symmetric (even Legendre functions, $p=0$ parity) symmetry block. The numbers of bound states found for the highest J level with this symmetry are also given.

To our surprise we found that the high angular momentum dissociation limit was insensitive to the details of the underlying potential, appearing to be determined almost entirely by the dissociation energy. Thus the three ab initio potentials, which have similar dissociation energies, gave similar high J results. All the potentials showed a strong isotope effect.

The variation in the number of bound states at the high J limit gives some indication of variation with potential. To investigate the nature of these states we performed $J=46$ H_3^+ calculations using the MBB potential for all four symmetry blocks given in our coordinates. Table 5 gives the binding energies of the bound states obtained in the calculations. We note that no evidence could be found for bound $p=1$ parity states – total parity is given by $(-1)^{J+p}$ – at this level of rotational excitation. Instead, the bound levels appear to be composed of (near) degenerate pairs of states. No attempt was made to converge energies of the excited states. Thus to the accuracy of our calculations one cannot say whether the pairs given are degenerate (E′ symmetry) or split ($A_1'A_2'$ pairs).

At first sight, the lack of $p=1$ bound states is surprising, as one would expect the first rotationally ex-

Table 4
Calculated H_3^+ and H_2D^+ rotational near-dissociation levels. The dissociation energy, E_D, was taken as the sum of the electronic dissociation energy, E_D^{elec}, and a vibrational zero-point contribution

	Potential			
	DIM [8]	SDL [9]	MarB [10]	MBB [11]
E_D^{elec} (cm^{-1})	39713.4	37025.3	37171.8	37219.0
H_3^+ highest bound J				
J	50	46	46	46
number of bound states	2	3	2	4
$E_J(1)-E_D$ (cm^{-1})	−371.0	−480.6	−245.4	−595.9
H_3^+ lowest unbound J				
J	51	47	47	47
$E_J(1)-E_D$ (cm^{-1})	+429.4	+299.4	+588.0	+182.6
H_2D^+ highest bound J				
J	59	54	54	54
number of bound states	1	2	1	3
$E_J(1)-E_D$ (cm^{-1})	−226.2	−506.9	−219.8	−618.1
H_2D^+ lowest unbound J				
J	60	55	55	55
$E_J(1)-E_D$ (cm^{-1})	+481.6	+148.4	+458.4	+32.3

Table 5
Calculated frequencies, in cm^{-1}, relative to dissociation of the truly bound states of H_3^+ with $J=46$ for the MBB potential. All states have $p=0$ parity

$E_J(n)$	j even [a]	j odd [a]
1	−595.9	−596.9
2	−432.8	−425.3
3	−242.6	−290.2
4	−122.8	−28.0

[a] Parity of the Legendre functions used in the basis.

cited state of the vibrational ground state to be a $p=1$ level. For $J=46$, however, the rotational constants of the ν_0 level suggest that the separation between $K=46$ (which has $p=0$) and $K=45$ ($p=1$) levels should be more than 2000 cm^{-1}. One is forced to conclude that the levels in table 5 correspond to *vibrational* and not rotational excitation.

In conclusion we have performed variational, fully coupled rovibrational calculations on H_3^+ and H_2D^+ for a number of potentials. Given the accuracy of the ab initio potentials the high angular momentum dissociation limits can be taken with some confidence to be $J=46$ and $J=54$ for H_3^+ and H_2D^+ respectively. In this high angular momentum region, the low-lying excited states appear to be purely vibrational in nature.

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