Rotation-vibration states of H_3^+ at dissociation

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Calculations are presented which estimate energies for all the bound rotation-vibration energy levels of H_3^+ with rotation angular momentum $J=0$, 2 and 8. The calculations, which use Radau coordinates with z-axis of the molecule embedded perpendicular to the molecular plane, are performed on 128 nodes of a massively parallel computer. It is found that convergence with respect to basis set size of the higher J states is fairly slow and that further improvements are beyond the capabilities of the current computational set-up. © *2003 American Institute of Physics.*
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I. INTRODUCTION

A theoretical analysis of the near dissociation infrared spectrum of H_3^+, initially recorded by Carrington and co-workers[1] in 1983 and characterized experimentally by Carrington's group over the following decade,[2–4] remains one of the longest running problems in chemical physics. The challenge posed by this spectrum has stimulated many quantum mechanical studies of this system; see Refs. 5–7 for early examples. In particular a number of calculations have been successfully performed which characterize all the vibrational state of H_3^+ and, in some cases, the quasi-bound states too.[8–11] However it is well established that spectra recorded by Carrington and co-workers involve rotationally excited states of H_3^+ as the higher, dissociating states are quasibound states trapped by rotational barriers in the system.[12] The study of rotationally excited states of H_3^+ at its dissociation limit has received considerably less attention.

Calculations involving high-lying rotationally excited states have proved to be difficult for H_3^+. This is undoubtedly a consequence of both the strong Coriolis coupling found in this system and low-lying barrier to linear geometry. We will comment on further on these aspects of the problem below. A number of studies[13–15] have obtained results for rotationally excited of H_3^+ up to about $25\,000$ cm^{-1} or about two-thirds of the way to dissociation. Even at this energy, all these studies showed some problems with convergence. Only two previous quantum mechanical calculations have actually probed rotationally excited states of H_3^+ at the dissociation limit. Miller and Tennyson[16] studied the high J limit for the molecule and found that states with rotational quantum number J up to 45 could be bound for the system, in good agreement with semi-classical studies.[17] Conversely, Henderson and Tennyson[18] studied states with $J=1$ and 2 at dissociation but, despite runs on a mainframe lasting weeks, obtained very poorly converged results. In this work we present a method suitable for studying rotationally excited states of H_3^+ at dissociation, and give results for states with $J=2$ and

$J=8$. These calculations relied on the use of many nodes on a massively parallel computer.

II. METHOD

To calculate rotationally excited states we adapt the two-step procedure of Tennyson and Sutcliffe[19] which was already been successfully used to both calculate rotationally excited states of water at dissociation[20] and rotationally excited quasibound states of HOCl.[21] In this method the fully coupled rotation-vibration problem is solved by first solving a series of Coriolis-decoupled effective vibrational problems which assume the k, the project of J along the body-fixed z-axis, is a conserved quantity. The lowest solutions of these problems are then used as a basis for the fully coupled problem. This method has proved to be very efficient for calculating spectra of molecules with high levels of rotational excitation.[16,22] Furthermore the method has been parallelized such that, at least for fairly low values J, the computer time used only scales with $(J+1)$ when considering rotational states near dissociation.[20,23]

The efficiency of this two-step method depends on a good choice of the intermediate quantum number k. Most previous studies of H_3^+, e.g., Ref. 24, used a z-axis which lies in the plane of the molecule. However it is well-known[25,26] that the appropriate quantization axis for H_3^+ is the C axis which lies along the symmetry axis of the molecule and is perpendicular to the plane of the molecule. Following Sarkar *et al.*,[27] we have recently used an axis embedding which places the z-axis perpendicular to the plane of the molecule to perform a high accuracy study of the spectroscopically determined, i.e., low-lying, state of H_3^+.[28] This study showed that this z perpendicular embedding combined with the use of Radau coordinates to represent the vibrational motions had a number of advantages. Besides giving an appropriate intermediate quantization this method proved to be much more robust at treating linear geometries.

For H_3^+ the symmetry-related linear saddle points lie at only about one-third of the dissociation energy. In Jacobi

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coordinates these three saddle points correspond to geometries with $\theta=0$, $\theta=\pi$ and $R=0$. It is the third case where the atom-diatom stretching coordinate, R, goes to zero and θ becomes undefined that causes the problems.[9,29,30] Indeed the different rates of convergence for the different symmetries found in Jacobi coordinate studies of high lying rotationally excited states[13,15] can be directly attributed to difficulties encountered when treating this geometry. In Radau coordinates, except at very high energies, linear geometries can all be defined by considering cases with $\theta=0$ and $\theta=\pi$ only.

In this work we adapt the program PDVR3D,[23] designed to compute near dissociation states using massively parallel computers, to the z-perpendicular Radau coordinates used by us previously for low-lying states of H_3^+. This new program was run on the 576 processor Cray-T3E machine (Turing) which is managed as part of the CSAR service at the University of Manchester. It is important to note that this machine has 256 Mb memory on each node and a total wall-clock time limit of one day for large jobs.

PDVR3D tackles the vibrational part of the calculation by distributing angular grid points between nodes. Most of the calculations reported here used $n_\gamma=32$ angular grid points spread over 128 nodes, i.e., 4 nodes and hence 1 Gb memory per angular grid point. The angular grid was based on Gauss-Jacobi integration and varied as a function of J and k, which is necessary to ensure the correct behavior at linear geometries.[27] The calculation then follows the following steps:

1. For each k and parity block:
   (a) Solve a two-dimensional (2D) vibrational problem for each angular grid point.
   (b) Select N_2 2D solutions as a basis for the 3D vibrational problem.
   (c) Construct $N_3 = n_\gamma \times N_2$ dimensional 3D Hamiltonian.
   (d) Diagonalize this Hamiltonian using PARPACK.[31]
   (e) Store M_3 wave functions, Ψ^k, as amplitudes on each grid point.
2. Use the Ψ^k to construct the off-diagonal in k matrix elements. Write these matrix elements to disk and discard Ψ_i^k when no longer needed.
3. Upon completion of the loop over k, read in matrix elements of the full Hamiltonian of size $(J+1-p)\times M_3$ and diagonalize using PEIGS.[32]

In practice storing more than M_3 solutions at step 1(e) allows a number of second step calculations to be performed and hence convergence with parameter M_3 to be tested without repeating the more time consuming first step calculation.

The radial motions were represented using a grid based on Morse oscillatorlike functions[33] defined, in atomic units, by $r_e=3.07$, $D_e=0.07$ and $\omega_e=0.0075$. A grid of 60 points was used which was found to stretch far enough to give a reasonable representation of the near dissociation functions. These parameters were optimized by performing a series of $J=0$ calculations which varied the Morse parameters and tested grids of 52, 54, 58 and 64 points. Convergence was established both by self-consistency checks and by comparison with calculations performed in Jacobi coordinates.[34] The calculations presented here were based on the use of N_3

$=9984$ which is sufficient to converge the energy levels to within about 1 cm^{-1}. We were able to perform larger calculations than this for $J=0$,[34] but the $J>0$ calculations require more local memory. This is due to the need to save wave functions in memory which are used to compute the matrix elements off-diagonal in k. This constraint meant that $N_3=9984$ was the largest $J>0$ problem that could be attempted with the present facility.

The size of the final Hamiltonian is determined by the

TABLE I. Convergence of H_3^+ energy levels, $E(M_3)$ in cm^{-1}, as a function of the number of "vibrational" wave functions, M_3, used to converge the full Hamiltonian for $J=2+$, $p=0$ and $N_3=9984$. The first level given is eigenvalue number 1677.

| $E(2944)$	$E(2816)-E(2688)$	$E(2944)-E(2816)$
34 717.479	1.065	0.946
34 720.384	1.020	0.592
34 733.629	1.299	0.944
34 737.140	0.908	0.860
34 739.221	1.008	0.814
34 742.988	1.160	0.885
34 756.774	1.221	0.826
34 760.576	0.879	0.703
34 769.199	1.212	0.935
34 773.767	0.880	0.718
34 781.153	0.885	0.920
34 784.935	0.894	0.882
34 791.576	0.726	0.612
34 793.855	0.722	0.778
34 798.987	0.946	0.798
34 805.360	0.789	0.687
34 809.166	0.780	0.693
34 810.496	0.759	0.607
34 812.462	0.769	0.755
34 825.355	0.736	0.683
34 831.606	0.765	0.668
34 832.935	0.727	0.749
34 839.338	0.844	0.916
34 840.140	0.955	0.742
34 856.070	0.886	0.680
34 857.203	0.644	0.695
34 858.409	0.730	0.658
34 864.837	0.956	0.926
34 869.370	0.816	0.804
34 870.273	1.420	1.006
34 874.471	0.933	0.966
34 883.080	0.908	0.737
34 893.027	0.887	0.574
34 895.563	0.757	0.896
34 899.952	0.862	0.650
34 905.545	0.663	0.651
34 911.372	1.099	0.881
34 912.915	1.035	0.729
34 920.013	0.689	0.622
34 925.164	0.581	0.687
34 927.248	0.651	0.856
34 930.092	0.776	0.756
34 937.396	0.758	0.807
34 943.172	0.637	0.606
34 955.507	0.852	0.683
34 958.546	0.599	0.706
34 958.810	1.195	0.818
34 966.211	0.971	0.782
34 973.056	1.052	1.073
34 976.519	0.917	0.637
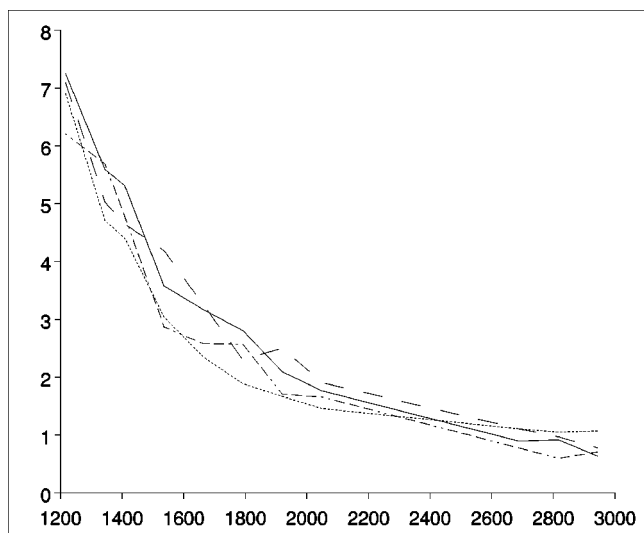
FIG. 1. Convergence of selected high-lying $J=2+p=0$ energy levels as functions M_3, where the size of the final Hamiltonian is given by $3 \times M_3$.

TABLE II. Convergence of H_3^+ energy levels, $E(M_3)$ in cm^{-1}, as a function of the number of "vibrational" wave functions, M_3, used to converge the full Hamiltonian for $J=8+$, $p=0$ and $N_3=9984$. The first level given is eigenvalue number 3808.

$E(2048)$	$E(1920) - E(1792)$	$E(2048) - E(1920)$
34 863.726	9.998	7.556
34 869.215	7.708	7.816
34 871.736	7.929	6.707
34 873.840	7.703	6.046
34 875.208	7.138	7.673
34 877.800	6.928	6.253
34 880.513	7.432	5.707
34 882.219	8.918	6.875
34 884.543	8.371	5.770
34 886.538	8.432	6.656
34 887.716	8.510	6.427
34 890.080	8.578	7.889
34 892.574	10.785	7.420
34 896.820	7.694	7.151
34 897.230	10.022	9.347
34901.023	9.595	7.029
34 901.956	9.579	7.174
34 904.727	7.668	6.748
34 907.020	8.652	8.001
34 909.334	9.394	6.801
34 913.085	8.260	7.157
34 914.163	7.927	7.455
34 916.648	9.285	7.246
34 917.956	9.305	7.862
34 921.865	7.146	7.010
34 922.814	8.136	7.301
34 924.025	8.809	6.730
34 925.570	9.645	8.582
34 928.456	8.804	7.454
34 934.108	7.416	8.658
34 936.202	8.539	6.977
34 939.376	8.164	6.703
34 940.386	8.557	6.270
34 940.731	8.487	7.747
34 942.442	9.786	7.712
34 945.154	8.430	6.846
34 946.629	7.527	7.037
34 949.781	8.830	7.922
34 950.673	9.098	8.094
34 955.958	9.553	7.548
34 956.961	10.702	8.927
34 960.738	9.524	7.575
34 962.887	8.303	8.330
34 964.650	9.879	7.541
34 968.040	8.626	8.730
34 971.452	8.927	8.661
34 974.436	9.657	6.953
34 978.208	9.179	7.503
34 979.281	7.660	8.614
34 981.636	9.743	7.508

number of first step solutions, M_3, retained for each k-block. For reasons of load balance[35] M_3 was taken to be independent of k. Our results proved to be strongly dependent on the choice of M_3 and convergence with respect to this parameter will be discussed below.

All calculations reported here used fit two of the global *ab initio* potential energy surface of Polyansky *et al.*,[36] which has a dissociation energy D_e of 37 170.4 cm^{-1} which corresponds to a D_0 value of 34 983 cm^{-1}. This surface, unlike the MBB potential[37] used in most previous studies of states near dissociation, is designed to have the correct shape at the dissociation limit. Calculations using this realistic potential are harder than those using the MBB surface because not only does the new surface support more vibrational states[34] but also many of the new vibrational states are very diffuse meaning that it is necessary to use much more extended radial basis sets. Some preliminary $J=0$ only results, which compared states for this potential with those for the MBB surface and tested the use of Radau coordinates, were reported previously.[34]

III. RESULTS

In this study we present results for two values of the rotational quantum number J. We selected $J=2$ as a low value for which tests could be performed without being too computationally expensive, and $J=8$ as lying in the $J=5-10$ range which is thought to be regime for the zero kinetic energy release near dissociation spectrum.[38] In practice the limit on total CPU time meant that converged first step calculations could not be performed for $J>8$ on the Turing computer.

Table I shows convergence of near-dissociation states with $J=2$, + vibrational parity[27,28] and $p=0$ rotational parity. Figure 1 similarly shows convergence of selected high-lying $J=2$ levels as a function of M_3. These results show that the convergence is slow and almost monotonic. For local memory reasons, the calculations with $M_3=2944$ were the

largest that could be attempted on Turing. These calculations converge the highest $J=2$ levels to 1 cm^{-1}. As is usual in variation calculations, the lower levels display much more rapid convergence.

Table II presents a similar convergence study for the $J=8+$, $p=0$ levels. In this case the maximum M_3 is 2048 as this was the largest value for which calculations were possible. As the size of the final Hamiltonian scales with $J+1-p$, the $J=8$ Hamiltonian matrix is three times the dimen-

TABLE III. Convergence of H_3^+ $J=2+$, $p=0$ rotational energy levels in the region of the barrier to linearity, $E(M_3)$ in cm^{-1}, as a function of the number of "vibrational" wave functions, M_3, used to converge the full Hamiltonian.

Level	$E(2048)$	$E(2048)-E(150)$	$E(2048)-E(200)$
41	10 704.567	0.255	0.201
42	10 770.235	0.313	0.275
43	10 898.110	0.271	0.228
44	10 908.532	0.139	0.134
45	11 026.466	1.553	1.228
46	11 042.115	1.686	1.581
47	11 105.118	3.553	3.483
48	11 305.428	0.118	0.093
49	11 427.514	0.285	0.216
50	11 529.816	0.256	0.193
51	11 575.797	0.118	0.114
52	11 683.375	0.737	0.574
53	11 769.228	0.787	0.639
54	11 807.408	0.466	0.435
55	11 884.705	1.037	0.954
56	11 944.639	0.497	0.417
56	11 944.639	0.497	0.417
57	12 023.318	0.504	0.438
58	12 148.858	0.716	0.546
59	12 222.023	0.504	0.399
60	12 300.365	0.293	0.253
61	12 381.264	0.244	0.232
62	12 453.805	4.535	3.871

TABLE IV. Convergence of H_3^+ $J=8+$, $p=0$ rotational energy levels in the region of the barrier to linearity, $E(M_3)$ in cm^{-1}, as a function of the number of "vibrational" wave functions, M_3, used to converge the full Hamiltonian.

Level	$E(2048)$	$E(2048)-E(150)$	$E(2048)-E(200)$
75	10 569.063	0.257	0.155
76	10 637.950	0.255	0.146
77	10 693.596	0.209	0.117
78	10 720.130	0.233	0.148
79	10 764.738	0.410	0.226
80	10 786.698	2.805	1.904
81	10 796.365	2.618	1.411
82	10 843.390	0.310	0.175
83	10 924.280	0.213	0.129
84	10 970.297	2.529	1.312
85	10 989.431	0.748	0.395
86	11 070.826	0.272	0.150
87	11 115.179	11.219	7.873
88	11 161.140	4.501	2.660
89	11 163.817	5.476	3.763
90	11 183.948	0.269	0.162
91	11 262.877	0.168	0.104
92	11 281.203	2.465	1.476
93	11 312.996	4.675	2.946
94	11 370.653	0.273	0.171
95	11 421.491	7.594	5.082
96	11 433.859	0.114	0.059
97	11 520.394	6.251	4.346
98	11 670.287	2.787	1.472
99	11 706.162	4.128	2.423
100	11 723.123	0.247	0.153
101	11 830.570	2.238	1.446
102	11 851.465	1.898	1.084
103	11 858.131	1.572	0.882
104	11 877.626	3.187	1.838
105	11 931.326	0.233	0.134
106	11 974.300	3.101	2.010
107	12 048.377	4.678	3.202
108	12 064.332	2.504	1.558
109	12 106.444	9.187	6.533
110	12 138.802	17.220	11.797
111	12 180.370	3.585	2.279
112	12 213.609	20.725	14.224
113	12 283.466	5.276	2.916
114	12 319.198	9.474	7.044
115	12 340.195	5.119	3.120
116	12 344.363	10.453	6.178
117	12 384.448	2.550	1.515
118	12 405.712	1.945	1.004
119	12 447.870	2.324	1.368

sion of the one with the same value of M_3 for $J=2$. The density of energy levels should approximately scale by the same amount. A full list of the $J=0$, $J=2+p=0$ and $J=8+p=0$ levels is provided in the journal's electronic archive.[39]

The convergence displayed by the $J=8$ results is again fairly slow and our largest calculations is only converged to within 10 cm^{-1} in the near dissociation region. Actually this number is surprisingly poor as for $J=2+,p=0$ with $M_3=2048$ the levels are converged to better than 2 cm^{-1}. Previous studies using the two-step procedure have assumed that the convergence obtained using as a function of M_3 does not depend strongly on J. The present calculations suggest that the results for $J=8$ with $M_3=2048$ have a convergence error approximately five times that of the results of $J=2$ with the same value of M_3.

Since these are the first calculations to probe the near dissociation region of H_3^+ with $J>2$ we wondered whether this slower convergence with increasing J was a property of the near dissociation region. To test this we performed several desktop calculations on the low-lying energy levels which are summarized in Table III. In these calculations we deliberately used small values of M_3 so that the rate of convergence could be assessed. These calculations showed that using $M_3=200$ converged the $J=8$ levels in the region of the barrier to linearity (10 500–12 500 cm^{-1}) on average to 2 cm^{-1} whereas for the $J=2$ level in the same region with $M_3=200$ the average convergence error is 0.6 cm^{-1}. Thus the convergence of the low-lying levels also shows differential convergence, although the factor between $J=2$ and $J=8$ is less than five which we found at dissociation. Such behavior has not been remarked on before. Whether it is a

feature of the z-perpendicular embedding or of H_3^+ rotational calculations in general is not entirely clear, but the fact that such behavior has not been seen previously suggests that it maybe a feature of the z-perpendicular embedding.

Our calculations show that the potential of Polyansky et al.[36] supports at least $684+$ (even) and $597-$ (odd) vibrational states with $J=0$. 1726 with $J=2+p=0$ and 3857 $J=8+p=0$ (Table IV). Therefore a full study of states up to $J=10$ will require the calculation of over 100 000 states once all symmetries are included. This is before consideration of the above dissociation quasibound states which provide the upper (and at least some lower) states in the near-dissociation spectrum observed by Carrington and co-workers.[2–4]

It has been remarked on before that H_3^+ is a particularly difficult molecule to obtain good convergence for because of the strong intermode and Coriolis couplings.[40] It is worth

comparing the present results with those obtained for the near dissociation vibration-rotation states of water, which has a somewhat deeper potential than H_3^+ and a fairly similar number of bound states. For water with $J = 0$ a calculation with $N_3 = 11\,520$ was found to converge all except the highest six vibrational states to better than 0.1 cm^{-1},[20] almost an order of magnitude better than the similar size calculation for H_3^+. Even more strikingly, the use of $M_3 = 1152$ converged the near dissociation $J = 2$ levels of water to within 0.4 cm^{-1} something that could not achieve with an H_3^+ calculation based on a Hamiltonian matrix of almost three times the dimension.

IV. CONCLUSIONS

The full quantum mechanical model of the H_3^+, infrared, near dissociation spectrum of Carrington and co-workers[2–4] has provided a challenge for theory for almost two decades. The calculations we report are the first to attempt full calculations of the rotational states of H_3^+ which are thought to be involved in this spectrum. These calculations proved to be at the limit of what was computationally possible to us with the facilities available. However high performance computing facilities are expanding rapidly. We believe the strategy outlined here augmented by developments which allow quasi-bound rotation-vibration states to be characterized[21] will provide the basis for a full simulation of this challenging spectrum.

A thorough analysis, meaning a complete model of the various experimental predissociation spectra, requires rather more than just energy levels as presented here and in most other quantal treatments of H_3^+ at dissociation. Lifetimes play a crucial role in determining what is observed experimentally.[3] Furthermore transitions are excited by a single laser photon and therefore are subject to dipole selection rules. We are currently working on these two aspects of the problem.

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