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Rotational Levels of H_2D^+: Variational Calculations and Assignments

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Rotational term values for the highly asymmetric H_2D^+ molecule are calculated variationally from first principles using an accurate potential energy surface. Fits are performed using the conventional Watson A-reduced and Padé forms of effective Hamiltonians. A sixth-order Padé fit gives satisfactory assignments for the vibrational ground state rotational levels up to $J = 25$, in contrast to previous studies, and assignments for levels up to $J = 30$. The behavior of conventional effective Hamiltonians for these levels is also discussed.

1. INTRODUCTION

The simple molecular ion H_3^+ and its isotopomers play fundamental role in many astrophysical processes (*1*). In recent years, its use as an astronomical probe has been aided by variational calculations (*2*) and effective Hamiltonian fits (*3–6*) of the rovibrational spectra.

This paper is motivated by two other reasons for understanding the spectrum of H_3^+ and its isotopomers. First, any step toward understanding the states of H_3^+ and its isotopomers with high angular momentum, J, and high vibrational excitation is important, since it is generally accepted (*7*) that the challenging Carrington–Kennedy spectrum (*8, 9*) consists of transitions between highly excited states. The second complementary reason is the importance of this ion for theoretical molecular spectroscopy. Since H_2D^+ is a very light asymmetric top, problems in both the assignment and fitting of its energy levels arise when using the effective Hamiltonian approach. Analogous problems are encountered in other H_2X molecules (X = O, S, Se) (*10–13*).

The availability of very accurate ab initio potential energy and dipole surfaces (due to MBB (*14*)) and the simplicity of the H_2D^+ ion mean that high quality variational calculations of its spectrum are possible. However the assignment of high-J energy levels of this system has proved very difficult (*15, 16*). Thus, an area of mutually beneficial cooperation between variational calculations and effective Hamiltonians arises; the first needs the second for assignment purposes, the second needs the first for the improvement of its theoretical models. The variational approach, described in Ref. (*17*), can calculate high-J energy levels. These levels give one the opportunity to test different effective Hamiltonian models in order to determine which is the best. To investigate the ability of, say, Padé approximated effective Hamiltonians (*10*) to give a reasonably good fit of high-J data is interesting both for the development of

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the theory of approximated effective Hamiltonians and for the assignment of variationally calculated high-J energy levels.

There is actually little available experimental data on the rotational transitions of H_2D^+. Laboratory observations of transitions 1_{10}–1_{11} (*18, 19*) and 2_{20}–2_{21} (*20*) have been published; the former has also been tentatively observed in the interstellar medium (*21*). A third transition 1_{01}–0_{00} has also been recorded in the laboratory (*22*). Although it is possible to estimate frequencies for some rotational transitions of H_2D^+ from differences between observed rovibrational frequencies, all the above transitions in fact relied heavily on comparisons with ab initio calculations for their assignment.

In a previous paper, Tennyson and Sutcliffe (*23*) presented variational calculations of the energy levels of H_2D^+ using the ab initio surface of Schinke *et al.* (*24*). In that work the ν_2 and ν_3 fundamental levels were too low by approximately 20 and 25 cm^{-1}, respectively, and specific assignment of the energy levels was not attempted. A subsequent attempt by Tennyson *et al.* (*15*) at assigning the rotational levels of H_2D^+, using a conventional effective Hamiltonian constants derived from calculations with $J \leqslant 4$, failed for $J > 11$. In contrast, a simple rigid dipole model was found sufficient to explain the pure rotational spectrum of H_2D^+, even for high J (*16*).

In the present paper we present variational calculations of H_2D^+ levels up to $J = 30$. These levels have much higher accuracy than the ones previously published (*23*). Assignment of the levels of the ground vibrational state are obtained for all calculated J values. Results and comparison of the fitting of the ground state energy levels to the effective Hamiltonians in the conventional (*25*) and Padé (*10*) form are presented.

2. VARIATIONAL CALCULATIONS

These calculations were performed in scattering coordinates using the TRIATOM program suite (*26*) and the MBB potential energy surface (*14*). The calculations used the two-step variational procedure of Tennyson and Sutcliffe (*23*). The first, "vibrational" step, was converged using the lowest 800 basis functions selected on energy grounds. The basis set comprised products of previously optimised (*27*) Morse oscillator-like functions for the radial coordinates and associated Legendre functions for the angular coordinate.

The rotational calculations were performed with a basis of $300 \times (J+1)$ functions selected from the $J+1$ first-step calculations using an energy ordering criterion (*28*). Previous analysis suggested that this basis is sufficient to converge levels with $J = 15$ to about 0.1 cm^{-1} (*15*) and $J = 30$ to 1 cm^{-1} (*16*). This present work suggests that the latter figure is over optimistic, a point we return to below.

For test purposes, highly converged calculations were also performed for levels of the vibrational ground state with $J \leqslant 7$. These calculations used 1000 functions in the first step for each k block and $400 \times (J+1)$ functions for the second step. With these basis functions the rotational levels of the vibrational ground state were stable to adding further functions in either step of the calculation to better than 0.00001 cm^{-1}. However at this level it is difficult to be sure that one has eliminated other, larger, systematic numerical errors from the nuclear motion calculations.

3. ASSIGNMENT AND FITTING

Values for the assigned rotational energy levels with $J \leqslant 25$ are presented in Table I. These were assigned as follows. The levels up to $J = 8$ could be assigned immediately by comparing the variationally calculated levels with the levels predicted from the effective constants of Kozin *et al.* (*6*), which were obtained from fits of experimental data. Differences between the ground state and certain excited state levels with the same rotational quantum numbers, JK_aK_c, change smoothly with increasing J. This allowed us to predict with reasonable accuracy values for the levels with higher J using the known values for lower J's and thus step up the J ladder. Using the previously mentioned calculations and effective Hamiltonian calculations of already assigned levels, we obtained an internally consistent system of assigned levels up to $J = 25$.

The assignment of the levels with high K_a was not unambiguous for $J = 17$ and above. Furthermore, not all of the high-K_a levels were obtained in the variational calculations, due to the extensive intrusion of rotational levels belonging to vibrationally excited states. For this reason levels with high K_a were excluded from the fit and Table I.

In the present paper we are interested primarily in the results of fits to and predictions of H_2D^+ energy levels with high J for the ground vibrational state. The properties of the effective Hamiltonian models for other vibrational states are similar to those of the ground vibrational state, except for the Coriolis interaction terms, and we do not consider the fitting of excited vibrational states data here.

Several different effective Hamiltonian models for the assignment and fitting of variationally calculated levels were tried. The model with the terms up to J^4, which was sufficient for fitting the experimental data (*6*), was not flexible enough to fit the large set of variationally calculated levels considered here. Instead, a model with 15 constants in either conventional (*25*) or Padé (*10*) form with the terms up to J^6 was used for fit. The standard deviation of the best Padé model fit was half that of the conventional model.

Initially we thought that this ratio was too small for a fit of high-J levels of a light molecular ion. We therefore tested other molecules with the similar convergence properties of the effective Hamiltonian and with experimentally known high-J transitions, namely, H_2O in both the ground and the (010) vibrational state. For the bending fundamental of water, the standard deviation of a 24-parameter Borel model is 60 times smaller than the standard deviation of a conventional fit with the same number of parameters (*11*). Fitting the experimental data for water with a model of 15 parameters (terms up to J^6) resulted in a threefold improvement of the standard deviation of the fit in the Padé model compared to a conventional fit. This result is consistent with our observations on fitting of the variationally calculated H_2D^+ levels.

As found for other molecules, the increased accuracy of the prediction of high-J levels, which were not included in the fit, is more dramatic. Table II presents energy levels of H_2D^+ from $J = 26$ to 30 from the variational calculations and calculated using the effective Hamiltonian constants presented in Table III. These constants were obtained by fitting the levels up to $J = 25$ in the Padé model of 15 parameters. Table II shows that the maximum error in the predicted levels is around 300 cm^{-1}. The analogous conventional model calculations gives errors of up to 6000 cm^{-1}.

How can one improve the fit to account for discrepancy of up to 300 cm^{-1} between the predictions from the Padé model and the variational calculations? It is tempting to expand the model to include terms up to J^8. However, our attempts to do this show that the accuracy of the variationally calculated levels does not warrant this treatment. In particular, the use of a 24-parameter model gave only a minor improvement over the 15-parameter fit.

A second possibility is to try to improve the variational calculations. To this end we performed a series of further convergence tests on the $J = 30$ levels. These tests

TABLE I

Comparison of Variationally Calculated and Fitted Rotational Term Values, in cm^{-1}, for the H_2D^+ Vibrational Ground State for Levels Used in the Fit

JK_aK_c	calc	fit	c−f	JK_aK_c	calc	fit	c−f
1 0 1	45.6780	45.6054	0.0725	7 1 7	1048.7090	1048.9177	−0.2087
1 1 1	60.0208	60.0291	−0.0083	7 1 6	1272.9624	1273.7294	−0.7670
1 1 0	72.4326	72.4227	0.0099	7 2 6	1273.6353	1274.3253	−0.6899
2 0 2	131.5940	131.4379	0.1561	7 2 5	1444.3321	1445.2127	−0.8805
2 1 2	138.8146	138.7112	0.1034	7 3 5	1455.4639	1456.0660	−0.6020
2 1 1	175.8586	175.7129	0.1457	7 3 4	1553.0744	1553.6006	−0.5262
2 2 1	218.6201	218.6841	−0.0641	7 4 4	1612.1715	1612.4676	−0.2962
2 2 0	223.8128	223.8397	−0.0269	7 4 3	1642.3398	1642.4710	−0.1311
3 0 3	251.3156	251.1040	0.2116	7 5 3	1775.5776	1775.7234	−0.1458
3 1 3	253.9687	253.7706	0.1981	7 5 2	1778.9315	1779.0163	−0.0849
3 1 2	326.0113	325.7844	0.2269	7 6 2	1968.6782	1968.6089	0.0693
3 2 2	354.6774	354.5994	0.0780	7 6 1	1968.8159	1968.7419	0.0740
3 2 1	376.2038	376.0192	0.1846	7 7 1	2194.4325	2193.8794	0.5531
3 3 1	458.2830	458.4120	−0.1291	7 7 0	2194.4345	2193.8813	0.5532
3 3 0	459.7634	459.8697	−0.1063	8 0 8	1327.5186	1328.0913	−0.5727
4 0 4	402.7254	402.4959	0.2295	8 1 8	1327.5290	1328.0904	−0.5695
4 1 4	403.5287	403.2925	0.2361	8 1 7	1585.5594	1586.7438	−1.1844
4 1 3	515.9304	515.7694	0.1610	8 2 7	1585.7429	1586.8689	−1.1260
4 2 3	531.1576	531.0468	0.1108	8 2 6	1792.7066	1794.1778	−1.4712
4 2 2	581.2355	580.9713	0.2641	8 3 6	1796.9534	1798.1017	−1.1483
4 3 2	645.4115	645.3638	0.0477	8 3 5	1937.7124	1939.0169	−1.3045
4 3 1	654.3211	654.1757	0.1454	8 4 5	1972.6346	1973.3966	−0.7620
4 4 1	778.5895	778.7504	−0.1609	8 4 4	2033.7760	2034.4875	−0.7115
4 4 0	778.9262	779.0785	−0.1523	8 5 4	2140.1334	2140.6304	−0.4970
5 0 5	586.0490	585.8682	0.1808	8 5 3	2151.7885	2152.1757	−0.3872
5 1 5	586.2660	586.0746	0.1914	8 6 3	2329.4465	2329.7861	−0.3396
5 1 4	738.4717	738.5280	−0.0563	8 6 2	2330.2756	2330.5957	−0.3200
5 2 4	744.8253	744.8393	−0.0140	8 7 2	2551.8543	2551.5610	0.2933
5 2 3	832.8702	832.7602	0.1100	8 7 1	2551.8803	2551.5861	0.2942
5 3 3	876.2906	876.2443	0.0463	8 8 1	2803.7600	2802.5504	1.2096
5 3 2	903.7496	903.5215	0.2282	8 8 0	2803.7603	2802.5507	1.2096
5 4 2	1012.1118	1012.0942	0.0176	9 0 9	1637.4792	1638.5015	−1.0224
5 4 1	1014.8004	1014.7325	0.0680	9 1 9	1637.4794	1638.5004	−1.0210
5 5 1	1177.2452	1177.3446	−0.0989	9 1 8	1928.4708	1930.0188	−1.5480
5 5 0	1177.3120	1177.4085	−0.0965	9 2 8	1928.5147	1930.0240	−1.5093
6 0 6	801.4296	801.3922	0.0374	9 2 7	2168.2111	2170.1888	−1.9777
6 1 6	801.4834	801.4374	0.0460	9 3 7	2169.6120	2171.3041	−1.6921
6 1 5	990.7389	991.1146	−0.3758	9 3 6	2351.3335	2353.4398	−2.1063
6 2 5	992.9447	993.2400	−0.2953	9 4 6	2368.4566	2369.7803	−1.3237
6 2 4	1123.1397	1123.4441	−0.3044	9 4 5	2469.3830	2470.9505	−1.5675
6 3 4	1147.5163	1147.6931	−0.1768	9 5 5	2545.2022	2546.1591	−0.9570
6 3 3	1205.5994	1205.5862	0.0132	9 5 4	2575.1143	2576.0231	−0.9088
6 4 3	1290.8364	1290.8589	−0.0225	9 6 4	2731.9371	2732.8477	−0.9106
6 4 2	1301.9038	1301.7962	0.1076	9 6 3	2735.3906	2736.2522	−0.8617
6 5 2	1454.0911	1454.0839	0.0072	9 7 3	2949.4032	2949.9337	−0.5305
6 5 1	1454.7454	1454.7204	0.0250	9 7 2	2949.5805	2950.1067	−0.5262
6 6 1	1650.6486	1650.5270	0.1216	9 8 2	3198.9051	3198.1181	0.7869
6 6 0	1650.6607	1650.5385	0.1222	9 8 1	3198.9095	3198.1225	0.7871
7 0 7	1048.6970	1048.9112	−0.2142	9 9 1	3473.4880	3471.4594	2.0287

TABLE I—*Continued*

$J K_a K_c$	calc	fit	c−f	$J K_a K_c$	calc	fit	c−f
9 9 0	3473.4881	3471.4594	2.0287	12 3 10	3460.841	3462.760	−1.919
10 0 10	1978.1079	1979.6438	−1.5359	12 3 9	3736.183	3738.842	−2.659
10 1 10	1978.1079	1979.6434	−1.5355	12 4 9	3736.872	3738.947	−2.075
10 1 9	2301.3414	2303.0917	−1.7503	12 4 8	3957.848	3961.368	−3.520
10 2 9	2301.3499	2303.0775	−1.7276	12 5 8	3968.231	3970.050	−1.818
10 2 8	2571.4399	2573.7477	−2.3078	12 5 7	4110.228	4113.624	−3.396
10 3 8	2571.8408	2573.9320	−2.0913	12 6 7	4169.984	4171.814	−1.830
10 3 7	2789.1782	2791.8632	−2.6851	12 6 6	4225.117	4227.578	−2.461
10 4 7	2796.1700	2798.0105	−1.8404	12 7 6	4372.691	4375.517	−2.826
10 4 6	2940.5369	2943.0597	−2.5228	12 7 5	4382.135	4384.962	−2.827
10 5 6	2987.4029	2988.8190	−1.4161	12 8 5	4603.066	4606.736	−3.670
10 5 5	3047.2000	3048.8706	−1.6706	12 8 4	4603.695	4607.479	−3.784
10 6 5	3174.5682	3176.0177	−1.4495	12 9 4	4867.457	4870.083	−2.626
10 6 4	3185.5181	3186.9137	−1.3956	12 9 3	4867.482	4870.117	−2.635
10 7 4	3386.1716	3387.7167	−1.5450	12 10 3	5160.119	5159.490	0.629
10 7 3	3387.0160	3388.5480	−1.5320	12 10 2	5160.137	5159.491	0.646
10 8 3	3631.1357	3631.6921	−0.5564	12 11 2	5472.089	5467.822	4.267
10 8 2	3631.1693	3631.7255	−0.5562	12 11 1	5472.115	5467.822	4.293
10 9 2	3904.7773	3903.1461	1.6313	12 12 1	5791.403	5788.561	2.842
10 9 1	3904.7805	3903.1468	1.6337	12 12 0	5791.460	5788.561	2.899
10 10 1	4198.2850	4195.4553	2.8297	13 0 13	3178.620	3181.725	−3.105
10 10 0	4198.2851	4195.4553	2.8298	13 1 13	3178.621	3181.725	−3.104
11 0 11	2348.8858	2350.9659	−2.0801	13 1 12	3594.389	3594.533	−0.144
11 1 11	2348.8862	2350.9660	−2.0798	13 2 12	3594.389	3594.533	−0.144
11 1 10	2703.673	2705.342	−1.669	13 2 11	3945.921	3947.117	−1.196
11 2 10	2703.674	2705.332	−1.658	13 3 11	3945.921	3947.071	−1.150
11 2 9	3002.446	3004.799	−2.353	13 3 10	4246.210	4248.112	−1.902
11 3 9	3002.541	3004.748	−2.206	13 4 10	4246.356	4247.851	−1.495
11 3 8	3250.575	3253.473	−2.898	13 4 9	4496.416	4499.491	−3.074
11 4 8	3252.988	3255.133	−2.145	13 5 9	4500.030	4501.525	−1.495
11 4 7	3438.666	3441.949	−3.284	13 5 8	4683.709	4687.554	−3.845
11 5 7	3462.966	3464.715	−1.749	13 6 8	4715.957	4717.428	−1.471
11 5 6	3561.755	3564.323	−2.567	13 6 7	4808.534	4811.575	−3.041
11 6 6	3654.967	3656.763	−1.796	13 7 7	4918.851	4921.556	−2.705
11 6 5	3682.348	3684.253	−1.905	13 7 6	4942.461	4945.354	−2.893
11 7 5	3861.089	3863.488	−2.399	13 8 6	5140.799	5145.297	−4.498
11 7 4	3864.216	3866.591	−2.375	13 8 5	5143.414	5147.882	−4.468
11 8 4	4099.505	4101.724	−2.219	13 9 5	5396.956	5401.812	−4.856
11 8 3	4099.681	4101.902	−2.221	13 9 4	5397.066	5401.969	−4.903
11 9 3	4369.751	4369.967	−0.216	13 10 4	5685.093	5687.538	−2.444
11 9 2	4369.754	4369.973	−0.219	13 10 3	5685.094	5687.544	−2.450
11 10 2	4664.250	4661.428	2.822	13 11 3	5996.929	5995.057	1.872
11 10 1	4664.267	4661.428	2.839	13 11 2	5997.122	5995.057	2.065
11 11 1	4972.733	4969.455	3.278	13 12 2	6323.013	6317.389	5.624
11 11 0	4972.733	4969.455	3.278	13 12 1	6323.078	6317.389	5.689
12 0 12	2749.256	2751.871	−2.615	13 13 1	6648.945	6648.152	0.793
12 1 12	2749.256	2751.871	−2.615	13 13 0	6648.945	6648.152	0.793
12 1 11	3134.896	3136.070	−1.174	14 0 14	3636.343	3639.867	−3.524
12 2 11	3134.896	3136.066	−1.170	14 1 14	3636.345	3639.867	−3.522
12 2 10	3460.826	3462.833	−2.007	14 1 13	4081.493	4079.963	1.530

TABLE I—*Continued*

JK_aK_c	calc	fit	c−f
14 2 13	4081.493	4079.964	1.529
14 2 12	4456.924	4456.830	0.094
14 3 12	4456.926	4456.810	0.116
14 3 11	4780.274	4780.858	−0.584
14 4 11	4780.284	4780.617	−0.333
14 4 10	5054.890	5056.855	−1.965
14 5 10	5055.849	5056.539	−0.690
14 5 9	5275.051	5278.566	−3.514
14 6 9	5289.110	5289.775	−0.665
14 6 8	5423.294	5427.807	−4.513
14 7 8	5497.143	5498.731	−1.588
14 7 7	5545.520	5548.330	−2.810
14 8 7	5711.434	5715.897	−4.463
14 8 6	5719.273	5723.603	−4.330
14 9 6	5955.557	5963.694	−8.137
14 9 5	5957.314	5964.300	−6.986
14 10 5	6238.218	6243.674	−5.456
14 10 4	6238.236	6243.705	−5.469
14 11 4	6547.356	6548.823	−1.467
14 11 3	6547.385	6548.824	−1.439
14 12 3	6875.548	6871.684	3.864
14 12 2	6875.575	6871.684	3.891
14 13 2	7211.833	7205.486	6.347
14 13 1	7211.838	7205.486	6.352
14 14 1	7540.134	7543.958	−3.824
14 14 0	7540.137	7543.958	−3.821
15 0 15	4121.758	4125.618	−3.860
15 1 15	4121.761	4125.618	−3.857
15 1 14	4595.516	4591.585	3.931
15 2 14	4595.516	4591.587	3.929
15 2 13	4992.916	4991.123	1.793
15 3 13	4992.917	4991.120	1.797
15 3 12	5337.616	5336.350	1.266
15 4 12	5337.626	5336.207	1.419
15 4 11	5633.565	5633.931	−0.366
15 5 11	5633.700	5633.154	0.546
15 5 10	5881.124	5883.433	−2.309
15 6 10	5885.938	5885.320	0.618
15 6 9	6063.423	6066.753	−3.330
15 7 9	6103.386	6103.623	−0.237
15 7 8	6187.403	6190.193	−2.790
15 8 8	6313.148	6316.725	−3.577
15 8 7	6332.736	6336.512	−3.776
15 9 7	6546.235	6554.484	−8.249
15 9 6	6550.002	6556.521	−6.518
15 10 6	6818.496	6826.312	−7.816
15 10 5	6818.631	6826.439	−7.808
15 11 5	7122.033	7127.029	−4.996
15 11 4	7122.033	7127.035	−5.002
15 12 4	7449.180	7448.896	0.284

JK_aK_c	calc	fit	c−f
15 12 3	7449.227	7448.896	0.331
15 13 3	7790.322	7784.705	5.617
15 13 2	7790.355	7784.705	5.650
15 14 2	8133.555	8127.840	5.715
15 14 1	8133.598	8127.840	5.758
15 15 1	8459.950	8472.104	−12.154
15 15 0	8459.956	8472.104	−12.148
16 0 16	4634.165	4638.292	−4.127
16 1 16	4634.169	4638.292	−4.123
16 1 15	5135.734	5128.628	7.106
16 2 15	5135.734	5128.630	7.104
16 2 14	5552.855	5549.153	3.702
16 3 14	5552.857	5549.158	3.699
16 3 13	5917.317	5913.739	3.578
16 4 13	5917.323	5913.679	3.644
16 4 12	6231.524	6230.538	0.986
16 5 12	6231.562	6229.928	1.634
16 5 11	6502.478	6502.475	0.003
16 6 11	6503.472	6501.101	2.371
16 6 10	6717.060	6719.527	−2.467
16 7 10	6734.210	6732.512	1.698
16 7 9	6860.065	6863.082	−3.017
16 8 9	6941.039	6945.458	−4.419
16 8 8	6985.556	6988.588	−3.032
16 9 8	7167.270	7173.047	−5.777
16 9 7	7173.271	7179.152	−5.881
16 10 7	7425.305	7434.219	−8.914
16 10 6	7430.946	7434.690	−3.744
16 11 6	7720.173	7727.957	−7.784
16 11 5	7720.274	7727.982	−7.708
16 12 5	8043.339	8046.761	−3.422
16 12 4	8043.458	8046.762	−3.304
16 13 4	8385.486	8383.062	2.424
16 13 3	8385.630	8383.062	2.568
16 14 3	8736.552	8729.850	6.702
16 14 2	8736.877	8729.850	7.027

JK_aK_c	calc	fit	c−f
16 15 2	9083	9081	2
16 15 1	9083	9081	2
16 16 1	9403	9429	−26
16 16 0	9403	9429	−26
17 0 17	5172	5177	−4
17 1 17	5172	5177	−4
17 1 16	5701	5690	11
17 2 16	5701	5690	11
17 2 15	6135	6130	5

TABLE I—*Continued*

JK_aK_c	calc	fit	c−f	JK_aK_c	calc	fit	c−f	JK_aK_c	calc	fit	c−f
17 3 15	6135	6130	5	18 12 6	9290	9298	−8	20 8 12	9886	9885	1
17 3 14	6518	6512	6	18 13 6	9628	9628	0	20 9 12	9902	9893	9
17 4 14	6518	6512	6	18 13 5	9628	9628	0	20 9 11	10012	10014	−2
17 4 13	6839	6846	−7	18 14 5	9979	9977	2	20 10 11	10103	10104	−1
17 5 13	6839	6846	−7	18 14 4	9979	9977	2	20 10 10	10134	10139	−5
17 5 12	7139	7137	3	18 15 4	10342	10337	5	20 11 10	10344	10341	3
17 6 12	7139	7135	5	18 15 3	10342	10337	5	20 11 9	10344	10345	−1
17 6 11	7380	7381	−1	19 0 19	6325	6331	−5	20 12 9	10609	10616	−7
17 7 11	7385	7382	4	19 1 19	6325	6331	−5	20 12 8	10609	10616	−7
17 7 10	7556	7557	−1	19 1 18	6905	6885	21	20 13 8	10926	10927	−1
17 8 10	7601	7599	2	19 2 18	6905	6885	21	20 13 7	10926	10927	−1
17 8 9	7676	7678	−2	19 2 17	7363	7358	6	20 14 7	11289	11267	22
17 9 9	7814	7818	−4	19 3 17	7363	7358	6	20 14 6	11289	11267	22
17 9 8	7830	7834	−4	19 3 16	7779	7769	11	21 0 21	7574	7582	−8
17 10 8	8056	8067	−11	19 4 16	7779	7769	11	21 1 21	7574	7582	−8
17 10 7	8061	8068	−7	19 4 15	8145	8131	15	21 1 20	8202	8170	32
17 11 7	8341	8350	−9	19 5 15	8145	8131	15	21 2 20	8202	8170	32
17 11 6	8341	8350	−9	19 5 14	8458	8451	7	21 2 19	8664	8668	−4
17 12 6	8657	8663	−6	19 6 14	8458	8450	8	21 3 19	8664	8668	−4
17 12 5	8657	8663	−6	19 6 13	8747	8732	15	21 3 18	9112	9100	12
17 13 5	8997	8998	−1	19 7 13	8747	8728	19	21 4 18	9112	9100	12
17 13 4	8997	8998	−1	19 7 12	8972	8970	2	21 4 17	9498	9481	17
17 14 4	9351	9347	4	19 8 12	8975	8967	8	21 5 17	9498	9481	17
17 14 3	9351	9347	4	19 8 11	9141	9138	3	21 5 16	9827	9822	5
17 15 3	9706	9703	3	19 9 11	9187	9181	6	21 6 16	9827	9822	5
17 15 2	9706	9703	3	19 9 10	9248	9255	−7	21 6 15	10141	10126	15
18 0 18	5737	5742	−5	19 10 10	9399	9402	−3	21 7 15	10141	10125	16
18 1 18	5737	5742	−5	19 10 9	9411	9416	−5	21 7 14	10405	10397	8
18 1 17	6291	6276	16	19 11 9	9640	9657	−17	21 8 14	10405	10391	14
18 2 17	6291	6276	16	19 11 8	9656	9658	−2	21 8 13	10633	10629	4
18 2 16	6739	6733	7	19 12 8	9940	9949	−9	21 9 13	10634	10620	14
18 3 16	6739	6733	7	19 12 7	9941	9949	−8	21 9 12	10787	10792	−5
18 3 15	7139	7131	9	19 13 7	10267	10271	−4	21 10 12	10825	10827	−2
18 4 15	7139	7131	9	19 13 6	10267	10271	−4	21 10 11	10887	10901	−14
18 4 14	7493	7480	14	20 0 20	6939	6945	−6	21 11 11	11047	11045	2
18 5 14	7493	7480	14	20 1 20	6939	6945	−6	21 11 10	11056	11059	−3
18 5 13	7791	7786	5	20 1 19	7543	7516	27	21 12 10	11284	11301	−17
18 6 13	7791	7785	7	20 2 19	7543	7516	27	21 12 9	11293	11302	−9
18 6 12	8052	8051	2	20 2 18	8006	8003	3	21 13 9	11585	11596	−11
18 7 12	8053	8048	5	20 3 18	8006	8003	3	21 13 8	11615	11596	19
18 7 11	8261	8262	−1	20 3 17	8437	8425	12	21 14 8	11923	11925	−2
18 8 11	8279	8274	5	20 4 17	8437	8425	12	21 14 7	11923	11925	−2
18 8 10	8395	8398	−3	20 4 16	8815	8798	17	22 0 22	8233	8242	−9
18 9 10	8484	8488	−4	20 5 16	8815	8798	17	22 1 22	8233	8242	−9
18 9 9	8522	8526	−4	20 5 15	9137	9129	8	22 1 21	8883	8845	38
18 10 9	8718	8723	−5	20 6 15	9137	9129	8	22 2 21	8883	8845	38
18 10 8	8722	8728	−6	20 6 14	9437	9423	14	22 2 20	9337	9353	−16
18 11 8	8979	8993	−14	20 7 14	9437	9421	16	22 3 20	9337	9353	−16
18 11 7	8983	8994	−11	20 7 13	9685	9681	4	22 3 19	9803	9792	11
18 12 7	9290	9298	−8	20 8 13	9685	9674	11	22 4 19	9803	9792	11

TABLE I—*Continued*

JK_aK_c	calc	fit	c−f	JK_aK_c	calc	fit	c−f	JK_aK_c	calc	fit	c−f
22 4 18	10194	10180	14	23 8 16	11853	11849	4	24 11 13	13436	13429	7
22 5 18	10194	10180	14	23 8 15	12116	12110	6	24 12 13	13487	13472	15
22 5 17	10526	10527	−1	23 9 15	12118	12103	15	24 12 12	13505	13523	−18
22 6 17	10526	10527	−1	23 9 14	12344	12338	6	24 13 12	13711	13692	19
22 6 16	10849	10839	10	23 10 14	12352	12321	31	24 13 11	13701	13698	3
22 7 16	10849	10839	10	23 10 13	12494	12504	−10	24 14 11	13985	13958	27
22 7 15	11128	11120	8	23 11 13	12520	12517	3	24 14 10	13985	13958	27
22 8 15	11128	11117	11	23 11 12	12588	12603	−15	25 0 25	10332	10357	−26
22 8 14	11374	11369	5	23 12 12	12699	12727	−28	25 1 25	10332	10357	−26
22 9 14	11374	11358	16	23 12 11	12747	12743	4	25 1 24	11045	10992	53
22 9 13	11588	11571	17	23 13 11	12984	12976	8	25 2 24	11045	10992	53
22 10 13	11595	11567	28	23 13 10	12984	12977	7	25 2 23	11428	11519	−91
22 10 12	11689	11695	−6	23 14 10	13287	13269	18	25 3 23	11428	11519	−91
22 11 12	11774	11771	3	23 14 9	13287	13269	18	25 3 22	11961	11967	−6
22 11 11	11801	11809	−8	24 0 24	9613	9630	−17	25 4 22	11961	11967	−6
22 12 11	11991	12004	−13	24 1 24	9613	9630	−17	25 4 21	12334	12358	−24
22 12 10	12020	12008	12	24 1 23	10305	10256	49	25 5 21	12334	12358	−24
22 13 10	12284	12278	6	24 2 23	10305	10256	49	25 5 20	12698	12711	−13
22 13 9	12299	12279	20	24 2 22	10719	10779	−60	25 6 20	12698	12711	−13
22 14 9	12610	12592	18	24 3 22	10719	10779	−60	25 6 19	12944	13033	−89
22 14 8	12610	12592	18	24 3 21	11228	11226	2	25 7 19	12944	13033	−89
23 0 23	8912	8925	−13	24 4 21	11228	11226	2	25 7 18	13314	13330	−16
23 1 23	8912	8925	−13	24 4 20	11613	11619	−6	25 8 18	13314	13330	−16
23 1 22	9584	9540	44	24 5 20	11613	11619	−6	25 8 17	13554	13602	−48
23 2 22	9584	9540	44	24 5 19	11960	11972	−12	25 9 17	13554	13602	−48
23 2 21	10022	10057	−35	24 6 19	11960	11972	−12	25 9 16	13876	13851	25
23 3 21	10022	10057	−35	24 6 18	12245	12293	−48	25 10 16	13878	13846	32
23 3 20	10508	10501	7	24 7 18	12245	12294	−49	25 10 15	14012	14077	−65
23 4 20	10508	10501	7	24 7 17	12579	12587	−8	25 11 15	14017	14055	−38
23 4 19	10899	10892	8	24 8 17	12579	12587	−8	25 11 14	14242	14257	−15
23 5 19	10899	10892	7	24 8 16	12846	12854	−8	25 12 14	14246	14238	8
23 5 18	11236	11244	−8	24 9 16	12846	12852	−6	25 12 13	14333	14353	−20
23 6 18	11236	11244	−8	24 9 15	13108	13096	12	25 13 13	14466	14429	37
23 6 17	11551	11562	−11	24 10 15	13116	13083	33	25 13 12	14503	14457	46
23 7 17	11551	11562	−11	24 10 14	13278	13302	−24	25 14 12	14695	14663	32
23 7 16	11853	11850	3	24 11 14	13288	13281	7				

Note. See Table III for the Constants used in the fit.

concentrated on the K_A even, K_C even symmetry block, which experience has shown to be the slowest to converge. Our calculations showed that while the $30_{0,30}$ level is converged to within 1 cm^{-1} as claimed previously (*16*), this is not so for the higher levels. In the worst case, $30_{10,20}$, we were able to lower the energy of this level by nearly 100 cm^{-1} by juggling with the parameters of the calculation. Other levels were lowered by between 10 and 50 cm^{-1}. This lowering of the levels, which is not encountered for low or intermediate values of J, actually worsens the agreement between the variational levels and the levels predicted from the fits as the latter levels are generally higher than

TABLE II

Comparison of Variationally Calculated and Fitted Rotational Term Values, in cm^{-1}, for the H_2D^+ Vibrational Ground State with $J > 25$

$J K_a K_c$	calc	fit	c−f	$J K_a K_c$	calc	fit	c−f	$J K_a K_c$	calc	fit	c−f
26 0 26	11071	11104	-33	27 9 18	15411	15364	47	29 2 28	14173	14129	44
26 1 26	11071	11104	-33	27 10 18	15413	15366	48	29 2 27	14388	14655	-267
26 1 25	11802	11748	54	27 10 17	15451	15603	-152	29 3 27	14388	14655	-267
26 2 25	11802	11748	54	27 11 17	15455	15602	-147	29 3 26	15022	15080	-58
26 2 24	12149	12277	-128	27 11 16	15822	15824	-2	29 4 26	15022	15080	-58
26 3 24	12149	12277	-128	27 12 16	15851	15808	43	29 4 25	15274	15435	-161
26 3 23	12707	12723	-16	27 12 15	15766	16025	-259	29 5 25	15276	15435	-159
26 4 23	12707	12723	-16	27 13 15	15763	15979	-216	29 5 24	15762	15752	10
26 4 22	13058	13110	-52	28 0 28	12601	12662	-61	29 6 24	15762	15752	10
26 5 22	13058	13110	-52	28 1 28	12601	12662	-61	29 6 23	15895	16049	-154
26 5 21	13450	13459	-9	28 1 27	13367	13317	50	29 7 23	15899	16049	-150
26 6 21	13450	13459	-9	28 2 27	13367	13317	50	29 7 22	16391	16334	57
26 6 20	13655	13779	-124	28 2 26	13628	13846	-218	29 8 22	16391	16334	57
26 7 20	13657	13779	-122	28 3 26	13628	13846	-218	29 8 21	16477	16610	-133
26 7 19	14062	14077	-15	28 3 25	14238	14280	-42	29 9 21	16479	16610	-131
26 8 19	14062	14077	-15	28 4 25	14238	14280	-42	29 9 20	16963	16873	90
26 8 18	14263	14353	-90	28 4 24	14527	14650	-123	29 10 20	16964	16873	91
26 9 18	14263	14354	-91	28 5 24	14527	14650	-123	30 0 30	14195	14300	-105
26 9 17	14642	14608	34	28 5 23	14984	14981	3	30 1 30	14195	14300	-105
26 10 17	14642	14607	35	28 6 23	14984	14981	3	30 1 29	14992	14961	31
26 10 16	14728	14841	-113	28 6 22	15131	15289	-158	30 2 29	14992	14961	31
26 11 16	14728	14831	-103	28 7 22	15131	15289	-158	30 2 28	15159	15482	-323
26 11 15	15062	15054	8	28 7 21	15602	15581	21	30 3 28	15161	15482	-321
26 12 15	15062	15020	42	28 8 21	15602	15581	21	30 3 27	15817	15893	-76
27 0 27	11827	11873	-46	28 8 20	15723	15858	-135	30 4 27	15817	15893	-76
27 1 27	11827	11873	-46	28 9 20	15723	15858	-135	30 4 26	16033	16229	-196
27 1 26	12577	12523	54	28 9 19	16185	16120	65	30 5 26	16031	16229	-198
27 2 26	12577	12523	54	28 10 19	16186	16121	65	30 5 25	16546	16527	19
27 2 25	12882	13053	-171	28 10 18	16385	16364	21	30 6 25	16546	16527	19
27 3 25	12882	13053	-171	28 11 18	16387	16366	21	30 6 24	16674	16810	-136
27 3 24	13467	13494	-27	28 11 17	16625	16589	36	30 7 24	16679	16810	-131
27 4 24	13467	13494	-27	28 12 17	16629	16588	41	30 7 23	17186	17087	99
27 4 23	13790	13875	-85	28 12 16	16765	16798	-33	30 8 23	17186	17087	99
27 5 23	13790	13875	-85	28 13 16	16803	16776	27	30 8 22	17249	17358	-109
27 5 22	14213	14216	-3	28 13 15	16899	16990	-91	30 9 22	17251	17358	-107
27 6 22	14213	14216	-3	28 14 15	16918	16931	-13	30 9 21	17745	17621	124
27 6 21	14385	14532	-147	29 0 29	13390	13471	-81	30 10 21	17745	17621	124
27 7 21	14385	14532	-147	29 1 29	13390	13471	-81	30 10 20	17692	17873	-181
27 7 20	14825	14828	-3	29 1 28	14173	14129	44	30 11 20	17689	17873	-184
27 8 20	14825	14828	-3					30 11 19	18198	18109	89
27 8 19	14985	15106	-121					30 12 19	18217	18111	106
27 9 19	14985	15107	-121								

Note. These levels were not used in the fit. See Table III for the constants used in the fit.

TABLE III

Rotational Constants, in cm^{-1}, for the Ground Vibrational State of H_2D^+

A	43.474823(765)	10^6 H_j	7.31372(726)
B	29.0823828(389)	10^6 H_{jk}	−34.2560(991)
C	16.5603378(354)	10^6 H_{kj}	61.268(336)
10^3 D_j	−9.3404577(323)	10^6 H_k	27.252(225)
10^3 D_{jk}	−0.26109(147)	10^6 h_j	4.36313(614)
10^3 D_k	−32.47629(222)	10^6 h_{jk}	35.683(527)
10^3 d_j	−3.805407(291)	10^6 h_k	27.252(225)
10^3 d_k	−24.93503(430)		

Note. These constants were obtained using a 15-parameter Padé fit to the variational results of Table I. Standard deviations are given in parentheses in units of the last decimal place.

the variational ones. It is likely that this behavior is caused by the onset of linear HDH^+ and HHD^+ geometries discussed below.

The role of linear geometries has been ignored up until now in the analysis of H_2D^+ rotational levels. The MBB potential (*14*), used in the present calculations, has a barrier to linearity of 14 275.5 cm^{-1}. Linear geometries are likely to have a profound effect on the structure of the rotational energy levels. However, previous calculations on high-lying vibrational levels of H_3^+ (*29*), recent experience with high-lying rotational levels of H_3^+ (*30*) and the $J = 30$ results above show that the basis functions used in this work are not well suited to treating linear geometries. Because the variational calculations are not reliable for these levels, it remains to be seen how the model Hamiltonians perform for levels strongly affected by linearity.

4. CONCLUSIONS

Rotational term values for the highly asymmetric H_2D^+ molecule have been calculated variationally from first principles. We have shown that by using the Padé form of an effective Hamiltonian, satisfactory assignments and fits can be obtained for vibrational ground state rotational levels up to $J = 25$. This is in contrast to previous studies on the same and similar data (*15, 16, 23*) which failed to even give vibrational assignments to states with $J > 11$. Indeed the present results show that the Padé model gives reasonable predictions for the energy levels with $J = 26$–30, where the effects of linear geometries are becoming increasingly important. Because the variational calculations are not yet reliable in this region, a full analysis of the very high-lying rotational levels of this system will have to await further theoretical (or indeed experimental) developments.

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