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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 $\nu_2$ and $\nu_3$ 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*

| $JK_aK_c$ | calc | fit | c−f | $JK_aK_c$ | 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 |
| 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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