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# Overtone Bands of $H_3^+$: First Principle Calculations

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Recent rovibrational calculations on an accurate *ab initio* potential energy surface for $H_3^+$ are extended for the overtone bands $2\nu_2$, $\nu_2 + \nu_1$, and $2\nu_1$. The computed energy levels are assigned, and rotational term values for the $H_3^+$ fundamentals are reported so that overtone and "hot band" spectra may be predicted.

## 1. INTRODUCTION

Since its spectrum was first observed by Oka (*1*) and Shy *et al.* (*2*) in 1980, $H_3^+$ and its isotopomers have excited considerable interest among experimental spectroscopists and theoretical chemists alike. All the infrared-allowed fundamentals of the ions have been characterized (*3–8*). The microwave spectrum of $H_2D^+$ has tentatively been observed in the interstellar gas cloud NGC 2264.

At the same time, there have been several *ab initio* studies of $H_3^+$ (*9–11*) which have led to attempts to calculate the experimentally observed vibration–rotation spectra from first principles (*11–16*). Recently, we have undertaken such calculations using a new *ab initio* surface due to Meyer *et al.* (*17*). Initial results for the vibration–rotation spectra of the fundamental bands confirmed the Meyer *et al.* prediction that their surface would give very good agreement with experiment.

In a previous paper (*18*), henceforth referred to as Paper I, the results for the fundamentals were given in the form of the molecular constants due to Watson (*3–8, 19*), to facilitate comparison with experiment. The rotational term values for $H_2D^+$ (*20*), $D_2H^+$ (*21*), and $D_3^+$ (*22*) have also been reported.

Despite the intensity of the theoretical and experimental activity, there are features in the infrared spectrum of $H_3^+$ that have still to be assigned (*23*). It is believed that these may be due to "hot bands," transitions from vibrationally excited states to higher energy vibrations, with relatively low values of the angular momentum quantum number, $J$. It is also possible that the hot band spectrum of $H_3^+$ could be a candidate for astronomical observation in molecular clouds that have been subjected to shocks (*24*).

For these reasons, and because the accuracy of our previous results for the fundamentals gives cause for confidence in our values for higher energy levels, we are presenting here results for the vibrational origins and rotational terms for the overtone bands of $H_3^+$. We also give rotational terms for the fundamental vibrations in order that the relevant hot band frequencies might be calculated.

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## 2. COMPUTATIONAL DETAILS

Eigenvalues for overtone bands of $H_3^+$ for $J = 0$–4 were calculated using scattering coordinates and the full vibration–rotation Hamiltonian developed by Tennyson and Sutcliffe (*11–16*) as reported in Paper I. The calculations were performed using programs SELECT, TRIATOM, and ROTLEV (*25*).

As before, the basis set was selected from the lowest 600 functions of a $J = 0$ calculation, and the rotationally excited levels were computed by using the 300 lowest vibrational levels for each $k = 0$–$J$ in the $J$ manifold under study. This two-step method of calculation enables accurate vibration–rotation energy levels to be calculated within the limitations of present computational facilities. All the results reported here were performed using the Cray 1s computers at the University of London Computing Centre.

There are three sources of error in our calculations that need to be considered, those due to the potential and those due to each of the two variational steps. Inaccuracies in the final energy levels due to inadequacies in the potential used are difficult to quantify other than by comparison with experiment.

In the first (vibrational) step of the calculation, the method of Tennyson and Sutcliffe is not adapted to the full $D_{3h}$ symmetry of $H_3^+$ (*15*). For this system basis functions with even angular components ($j$ even) are treated separately from those with odd ($j$ odd). For the modes of $H_3^+$ belonging to $E$ symmetry, one component of degenerate pairs of eigenvalues should be found with $j$ even and one with $j$ odd. But the present method can cause a splitting in these levels because only for full convergence are even and odd functions included on a completely equal footing.

An important test of accuracy is therefore the extent to which these $E$ pairs have identical energies. For the rotational levels of the fundamentals, the difference was never greater than 0.1 $cm^{-1}$, and usually of the order of 0.01 $cm^{-1}$. But the degeneracy was not so well represented for some overtone levels. In the worst case we found a difference of 1.3 $cm^{-1}$ for the $J = 4$, $K = 1$ level of $2\nu_1$, although most overtone $E$ components differed by less than half this amount.

Tests on the second step of the calculation in relation to the number of basis functions used showed that all levels reported here were converged to within 0.02 $cm^{-1}$.

## 3. RESULTS

The vibrational states of $H_3^+$ have been labeled using the quantum number $\nu_2$, which refers to the number of quanta of the bending mode associated with each group of vibrational bands. Members of a $\nu_2$ group are then associated with a second quantum number, $l_2 = -\nu_2, -\nu_2 + 2, \ldots, \nu_2 - 2, \nu_2$. The symmetry of the $H_3^+$ system then assigns levels with $l_2 = 0$ to $A_1$, those with $l_2 = \pm 3, \pm 6$, etc., to $A_1$, $A_2$ pairs, and all others to $E$. Table I summarizes the vibrational band origins ($J = 0$ calculations) up to $3\nu_2$.

Our previous experience with $H_3^+$ and its deuterated isotopomers suggests that the fundamentals are accurate to within 0.1%. The other band origins are probably only slightly less accurate, the error being due largely to inaccuracies in the potential energy surface.

TABLE I

Vibrational Band Origins ($J = 0$) for $H_3^+$ (in $cm^{-1}$)

|  | $v_2$ | $\ell_2 = 0$ | $\pm1$ | $\pm2$ | $\pm3$ |
|---|---|---|---|---|---|
| $\nu_2$ | 1 |  | 2521.28 E[a] |  |  |
| $\nu_1$ | 0 | 3178.35 $A_1$ |  |  |  |
| $2\nu_2$ | 2 | 4777.31 $A_1$ |  | 4997.68 E |  |
| $\nu_2+\nu_1$ | 1 |  | 5554.07 E |  |  |
| $2\nu_1$ | 0 | 6262.91 $A_1$ |  |  |  |
| $3\nu_2$ | 3 |  | 7010.49 E |  | 7296.49 $A_1$<br>7493.06 $A_2$ |

[a] Observed 2521.31 (3).

Within each $\nu_2$, $l_2$ vibrational manifold, the rotational levels may then be assigned on the basis of symmetry, using the quantum number $K$ for $A$ vibrational modes and $G$ for $E$ vibrational modes. Levels with $K/G = 0, 3, 6$, etc., have $A$ symmetry, and all others are $E$. A further quantum number $s$ distinguishes between rotational $A_1$ and $A_2$ modes. We note that occupation of levels with $A_1$ symmetry is forbidden as a result of nuclear spin statistics, but the energy levels from these states are included here for completeness.

The Tennyson/Sutcliffe (TS) method of calculating rovibrational levels labels the results for each $\nu$–$J$ manifold with $k$, $e/f$, and $j$. The significance of these labels has been discussed elsewhere (*15*). Levels with $j$ even correspond to $A_1$ or $E_x$ symmetry and $j$ odd levels to $A_2$ or $E_y$. For $A_1$ levels, the value of $s$ is given by $(-1)^J$, while for $A_2$ levels $s = (-1)^{(J+1)}$.

Finally, all levels are qualified by the superscript $'$ or $''$. This label relates to the total parity of the level given, in the TS scheme, by $(-1)^{J+p}$, where $p = 0$ denotes and $e$ level and $p = 1$ an $f$ level. Levels labeled $'$ have total parity even and those with $''$ have total parity odd. This parity is also given by $(-1)^K$.

Full values for the rotational terms of the vibrational ground state, $\nu_1$ and $\nu_2$, are presented in Tables II and III. For these bands, assignment to $A$ or $E$ was made easy by the fact the $E$ components differed in energy by 0.1 $cm^{-1}$ or less in all cases. For this reason, the $E$ components are not reported separately.

Rotational terms and vibrational band origins for $2\nu_2$, $\nu_2 + \nu_1$, and $2\nu_1$ are given in Tables IV–VI. Here we have presented both components of the $E$ modes. Assignment of the bands is more difficult not only because the $E$ components are not as close in energy as in the case of the fundamentals, but because there is considerable overlap of the rotational manifolds of the different vibrational states. This is particularly the case for the $l_2 = 0$ and $l_2 = \pm2$ terms in $2\nu_2$, where overlap commences at $J = 2$, and for $2\nu_1$, which overlaps with $3\nu_2$ for $J = 4$. Thus, we have given a full assignment of each band to avoid any ambiguity.

TABLE II

Rotational Term Values for $H_3^+$ (in cm$^{-1}$): Ground State and $\nu_1$

| | | Ground State | | | | $\nu_1$ |
|---|---|---|---|---|---|---|
| | | Expt. | Theory | | | Theory |
| Level J K s | | [3] | This work | [15] | [9] | This work |
| 1 0 | $A_2'$ | 86.96 | 86.93 | 86.87 | 87.24 | 84.84 |
| 1 1 | $E''$ | 64.12 | 64.10 | 64.05 | 64.30 | 64.47 |
| 2 0 | $A_1'$ | | 259.81 | 259.62 | 260.67 | 253.55 |
| 2 1 | $E''$ | 237.35 | 237.28 | 237.09 | 238.04 | 231.49 |
| 2 2 | $E'$ | 169.27 | 169.25 | 169.08 | 169.78 | 164.83 |
| 3 0 | $E''$ | 516.88 | 516.71 | 516.30 | 518.66 | 514.27 |
| 3 1 | $A_2'$ | 494.76 | 494.61 | 494.20 | 496.44 | 482.64 |
| 3 2 | $E'$ | 427.99 | 427.88 | 427.52 | 429.38 | 417.32 |
| 3 3 +1 | $A_2''$ | 315.29 | 315.25 | 314.93 | 316.30 | 306.93 |
| 3 3 -1 | $A_1''$ | | 315.26 | 314.95 | 316.30 | 306.96 |
| 4 0 | $A_1'$ | | 854.88 | 854.14 | | 834.33 |
| 4 1 | $E''$ | 833.57 | 833.31 | 832.60 | | 813.24 |
| 4 2 | $E'$ | 768.44 | 768.23 | 767.56 | | 749.61 |
| 4 3 -1 | $A_2''$ | 658.67 | 658.50 | 657.92 | | 642.28 |
| 4 3 +1 | $A_1''$ | | 658.43 | 657.85 | | 642.11 |
| 4 4 | $E'$ | 501.94 | 501.88 | 501.37 | | 488.67 |
| Band origin | | | | | | 3178.35 |

Two features of the $2\nu_2$, $l_2 = \pm 2$ manifold need further comment. First, the lowest rotational energy level for each value of $J$, for which $G = J + 2$, is lower than might be expected by comparison with the corresponding level in the $\nu_2 = 1$ manifolds ($\nu_2$ or $\nu_2 + \nu_1$, for example). In fact the rotational term is slightly negative for the $A_2''$ mode of $J = 1$ (i.e., the computed energy levels lie slightly below the vibrational band origin).

We attribute this feature to the more complicated character of the perturbative Hamiltonian due to Watson for values of $\nu_2 = 2$ ($l_2 = 0, \pm 2$) (*19*). In this case it is

TABLE III

Rotational Term Values for $H_3^+$ (in cm$^{-1}$): $\nu_2$ ($K$ is given by $G - U$)

| | | | | F(J,G,U=−1) | | | F(J,G,U=+1) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Expt. | Theory | | Expt. | Theory | |
| | | | | [3] | This work | [15] | [3] | This work | [15] |
| Level | | | | | | | | | |
| J | G | s | | | | | | | |
| 1 | 0 | +1 | $A_2''$ | 95.28 | 95.21 | 93.6 | | | |
| 1 | 0 | −1 | $A_1''$ | | 105.90 | 104.8 | | | |
| 1 | 1 | | $E'$ | | | | 88.13 | 88.09 | 87.0 |
| 1 | 2 | | $E''$ | | | | 26.73 | 26.76 | 25.8 |
| 2 | 0 | +1 | $A_1''$ | | 259.80 | 257.9 | | | |
| 2 | 0 | −1 | $A_2''$ | 291.45 | 291.36 | 290.8 | | | |
| 2 | 1 | | $E'$ | 234.15 | 234.01 | 231.7 | 268.93 | 268.85 | 268.2 |
| 2 | 2 | | $E''$ | | | | 202.53 | 202.48 | 201.7 |
| 2 | 3 | +1 | $A_1'$ | | | | | 92.69 | 92.0 |
| 2 | 3 | −1 | $A_2'$ | | | | 92.81 | 92.86 | 92.1 |
| 3 | 0 | +1 | $A_2''$ | 504.55 | 504.25 | 502.0 | | | |
| 3 | 0 | −1 | $A_1''$ | | 565.87 | 566.2 | | | |
| 3 | 1 | | $E'$ | 481.49 | 481.21 | 478.9 | 542.06 | 541.91 | 542.1 |
| 3 | 2 | | $E''$ | 409.93 | 409.72 | 407.5 | 471.00 | 470.88 | 470.7 |
| 3 | 3 | +1 | $A_2'$ | | | | 355.38 | 355.31 | 354.8 |
| 3 | 3 | −1 | $A_1'$ | | | | | 356.09 | 355.6 |
| 3 | 4 | | $E''$ | | | | 197.98 | 198.03 | 197.6 |
| 4 | 0 | +1 | $A_1''$ | | 825.81 | 822.9 | | | |
| 4 | 0 | −1 | $A_2''$ | 925.64 | 925.40 | 1030.0 | | | |
| 4 | 1 | | $E'$ | 804.70 | 804.25 | 801.5 | 901.71 | 901.48 | 902.9 |
| 4 | 2 | | $E''$ | 738.78 | 738.39 | 735.73 | 829.95 | 829.74 | 830.8 |
| 4 | 3 | +1 | $A_1'$ | | 623.23 | 620.7 | | 709.85 | 710.3 |
| 4 | 3 | −1 | $A_2'$ | 623.81 | 623.52 | 620.9 | 711.91 | 711.75 | 712.1 |
| 4 | 4 | | $E''$ | | | | | 547.73 | 547.6 |
| 4 | 5 | | $E'$ | | | | | 342.44 | 342.4 |
| Band origins | | | | | | | 2521.31 | 2521.28 | 2494 |

TABLE IV

Rotational Term Values for $H_3^+$: $2\nu_2$ and $2\nu_1$ $l_2 = 0$ States

| J | K | k | s | j | | $2\nu_2$ | $2\nu_1$ |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 1f | | o | $A_1'$ | 82.8 | 91.8 |
| | 1 | 0e | | e | $E''$ | 60.9 | 64.2 |
| | 1 | 1e | | o | | 60.8 | 64.1 |
| 2 | 1 | 2f | | e | $E''$ | 226.2 | 245.3 |
| | 1 | 1f | | o | | 226.0 | 244.9 |
| | 2 | 0e | | e | $E'$ | 160.7 | 164.5 |
| | 2 | 1e | | o | | 160.5 | 164.3 |
| | 0 | 2e | | e | $A_1'$ | 247.8 | 270.6 |
| 3 | 0 | 3f | | o | $A_2'$ | 492.7 | 527.1 |
| | 2 | 2f | | e | $E'$ | 407.5 | 432.4 |
| | 2 | 1f | | o | | 407.3 | 432.4 |
| | 3 | 0e | -1 | e | $A_1''$ | 299.1 | 301.2 |
| | 3 | 1e | +1 | o | $A_2''$ | 298.9 | 300.6 |
| | 1 | 2e | | e | $E''$ | 471.4 | 503.7 |
| | 1 | 3e | | o | | 471.5 | 504.0 |
| 4 | 1 | 4f | | e | $E''$ | 794.9 | 832.8 |
| | 1 | 3f | | o | | 794.3 | 831.5 |
| | 3 | 2f | +1 | e | $A_1''$ | 626.9 | 653.9 |
| | 3 | 1f | -1 | o | $A_2''$ | 626.8 | 653.9 |
| | 4 | 0e | | e | $E'$ | 476.1 | 438.7 |
| | 4 | 1e | | o | | 475.8 | 438.5 |
| | 2 | 2e | | e | $E'$ | 732.4 | 766.4 |
| | 2 | 3e | | o | | 732.1 | 765.6 |
| | 0 | 4e | | e | $A_1'$ | 815.3 | 853.7 |

necessary to consider off-diagonal terms in the Hamiltonian which couple levels with $l_2$ differing by 2, i.e., $l_2 = 0$ to $l_2 = \pm 2$.

The second feature that needs comment is the ordering of the $K$ values in the $l_2 = \pm 2$ manifold. For $\nu_2 = 1$, the rotational levels are labeled with a value of $K$ that

TABLE V

Rotational Term Values for $H_3^+$: $\nu_2 + \nu_1$ $l_2 = \pm 1$

| J | K | G | U | k | s | j | ω | s | j | ω |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1 | +1 | $1^f$ |  | o $E_y'$ | 86.3 |  | e $E_x'$ | 85.9 |
|  | 1 | 2 | +1 | $0^e$ |  | e $E_x''$ | 30.0 |  | o $E_y''$ | 30.0 |
|  | 1 | 0 | -1 | $1^e$ | +1 | o $A_2''$ | 90.3 | -1 | e $A_1''$ | 100.0 |
| 2 | 1 | 0 | -1 | $2^f$ | +1 | e $A_1''$ | 252.6 | -1 | o $A_2''$ | 280.7 |
|  | 1 | 2 | +1 | $1^f$ |  | o $E_y''$ | 201.6 |  | e $E_x''$ | 201.9 |
|  | 2 | 3 | +1 | $0^e$ | +1 | e $A_1'$ | 99.8 | -1 | o $A_2'$ | 99.8 |
|  | 2 | 1 | -1 | $1^e$ |  | o $E_y'$ | 224.4 |  | e $E_x'$ | 224.8 |
|  | 0 | 1 | +1 | $2^e$ |  | e $E_x'$ | 261.8 | -1 | o $E_y'$ | 261.2 |
| 3 | 0 | 1 | +1 | $3^f$ |  | o $E_y'$ | 526.4 |  | e $E_x'$ | 526.3 |
|  | 2 | 1 | -1 | $2^f$ |  | e $E_x'$ | 469.2 |  | o $E_y'$ | 469.5 |
|  | 2 | 3 | +1 | $1^f$ | +1 | o $A_2'$ | 355.9 | -1 | e $A_1'$ | 357.0 |
|  | 3 | 4 | +1 | $0^e$ |  | e $E_x''$ | 211.1 |  | o $E_y''$ | 210.9 |
|  | 3 | 2 | -1 | $1^e$ |  | o $E_y''$ | 395.3 |  | e $E_x''$ | 395.3 |
|  | 1 | 2 | +1 | $2^e$ |  | e $E_x''$ | 461.5 |  | o $E_y''$ | 461.6 |
|  | 1 | 0 | -1 | $3^e$ | +1 | o $A_2''$ | 493.1 |  | e $A_1''$ | 548.5 |
| 4 | 1 | 0 | -1 | $4^f$ | +1 | e $A_1''$ | 810.3 | -1 | o $A_2''$ | 898.8 |
|  | 1 | 2 | +1 | $3^f$ |  | o $E_y''$ | 808.6 |  | e $E_x''$ | 808.8 |
|  | 3 | 2 | -1 | $2^f$ |  | e $E_x''$ | 722.5 |  | o $E_y''$ | 721.9 |
|  | 3 | 4 | +1 | $1^f$ |  | o $E_y''$ | 551.5 |  | e $E_x''$ | 551.8 |
|  | 4 | 5 | +1 | $0^e$ |  | e $E_x'$ | 367.2 |  | o $E_y'$ | 367.0 |
|  | 4 | 3 | -1 | $1^e$ | -1 | o $A_2'$ | 604.0 | +1 | e $A_1'$ | 604.4 |
|  | 2 | 3 | +1 | $2^e$ | +1 | e $A_1'$ | 698.2 | -1 | o $A_1'$ | 700.3 |
|  | 2 | 1 | -1 | $3^e$ |  | o $E_y'$ | 787.8 |  | e $E_x'$ | 788.1 |
|  | 0 | 1 | +1 | $4^e$ |  | e $E_x'$ | 876.4 |  | o $E_y'$ | 876.4 |

corresponds exactly to the ordering of the $\nu_2 = 0$ levels (ground state, $\nu_1$). The value of $G$ is then obtained by adding $U$ ($= -l_2$) to the value of $K$. In this way, rotational energies increase with decreasing $G$, with $U = +1$ labeling the upper level and $U = -1$ the lower.

TABLE VI

Rotational Term Values for $H_3^+$: $2\nu_2\ l_2 = \pm 2$

| J | K | G | U | k | s | j | | ω | s | j | | ω |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 2 | +2 | $1^f$ | | o | $E_y'$ | 89.6 | | e | $E_x'$ | 89.3 |
| | 1 | 3 | +2 | $0^e$ | -1 | e | $A_1''$ | 1.0 | +1 | o | $A_2''$ | -3.2 |
| | 1 | 1 | -2 | $1^e$ | | o | $E_y''$ | 127.0 | | e | $E_x''$ | 127.1 |
| 2 | 1 | 1 | -2 | $2^f$ | | e | $E_x''$ | 306.8 | | o | $E_y''$ | 306.6 |
| | 1 | 3 | +2 | $1^f$ | -1 | o | $A_2''$ | 183.1 | +1 | e | $A_1''$ | 171.6 |
| | 2 | 4 | +2 | $0^e$ | | e | $E_x'$ | 34.6 | | o | $E_y'$ | 34.5 |
| | 0 | 2 | +2 | $1^e$ | | o | $E_y'$ | 268.0 | | e | $E_x'$ | 268.6 |
| | 2 | 0 | -2 | $2^e$ | +1 | e | $A_1'$ | 292.0 | -1 | o | $A_2'$ | 288.5 |
| 3 | 2 | 0 | -2 | $3^f$ | +1 | o | $A_2'$ | 568.9 | -1 | e | $A_1'$ | 553.6 |
| | 0 | 2 | +2 | $2^f$ | | e | $E_x'$ | 535.3 | | o | $E_y'$ | 535.6 |
| | 2 | 4 | +2 | $1^f$ | | o | $E_y'$ | 301.2 | | e | $E_x'$ | 301.4 |
| | 3 | 5 | +2 | $0^e$ | | e | $E_x''$ | 107.7 | | o | $E_y''$ | 107.5 |
| | 1 | 3 | +2 | $1^e$ | +1 | o | $A_2''$ | 433.0 | -1 | e | $A_1''$ | 454.6 |
| | 3 | 1 | -2 | $2^e$ | | e | $E_x''$ | 488.2 | | o | $E_y''$ | 487.9 |
| | 1 | 1 | -2 | $3^e$ | | o | $E_y''$ | 575.4 | | e | $E_x''$ | 575.4 |
| 4 | 1 | 1 | -2 | $4^f$ | | e | $E_x''$ | 933.6 | | o | $E_y''$ | 933.3 |
| | 3 | 1 | -2 | $3^f$ | | o | $E_y''$ | 848.2 | | e | $E_x''$ | 848.3 |
| | 1 | 3 | +2 | $2^f$ | +1 | e | $A_1''$ | 781.1 | -1 | o | $A_2''$ | 812.7 |
| | 3 | 5 | +2 | $1^f$ | | o | $E_y''$ | 462.6 | | e | $E_x''$ | 462.8 |
| | 4 | 6 | +2 | $0^e$ | | e | $E_x'$ | 253.6 | | o | $E_y'$ | 253.2 |
| | 2 | 4 | +2 | $1^e$ | | o | $E_y'$ | 654.4 | | e | $E_x'$ | 654.6 |
| | 4 | 2 | -2 | $2^e$ | | e | $E_x'$ | 718.4 | | o | $E_y'$ | 717.9 |
| | 0 | 2 | +2 | $3^e$ | | o | $E_y'$ | 889.7 | | e | $E_x'$ | 890.4 |
| | 2 | 0 | -2 | $4^e$ | +1 | e | $A_1'$ | 938.3 | -1 | o | $A_2'$ | 898.3 |

For the manifolds with $l_2 = \pm 2$ it is, however, necessary to permute the order of the $K$ values in order correctly to assign $A$ modes to $G = 0, 3, 6$, etc. and $E$ modes to the other values of $G$ and to arrive at the correct energy ordering.

A good example of this is comparison of the levels $G = 0$, $U = -2$ and $G = 2$, $U = +2$ for $J = 4$. Permuting the assignment of levels from $K = 2$ and $K = 0$ in this instance, the $A$ modes are correctly assigned to $G = 0$, while $E$ symmetry is assigned to components that differ only by 1 $\text{cm}^{-1}$.

There is, however, one remaining complication as far as the $G/U$ labeling scheme is concerned, which arises from the fact that $G = |K + U|$. Again, looking at the $J = 4$ manifold for $l_2 = \pm 2$, this gives rise to a situation in which there are two levels labeled with $G = 1$, $U = -2$. This means that any attempt to fit these levels will have to use the full Watson Hamiltonian (*19*), which depends explicitly on the values of $K$, $\nu_2$, $l_2$, and $s$, rather than any of the later versions formulated in terms of $G$ and $U$ (*3*).

## 4. CONCLUSIONS

We have reported overtone band origins and rotational term values for $H_3^+$. It is hoped that the results will prove useful in the identification of already observed features of the ion's infrared spectrum, and in indicating where new lines might be found for both laboratory and astronomical investigation. Similar results for the deuterated isotopomers of $H_3^+$ may be obtained from the authors.

Since the eigenvalues are well converged with respect to the number of basis functions used in the second step of the calculation, we suggest that the best estimate of the accuracy of the energy levels we have computed be the extent of nondegeneracy in the $E$ modes of each individual $\nu$–$J$ manifold.

The frequencies of allowed transitions may be computed using the selection rules $E \leftrightarrow E$, $A_2 \leftrightarrow A_2$, with $\Delta J = 0, \pm 1$ and $' \leftrightarrow ''$. Line strengths may also be calculated by computing transition moments for the eigenfunctions concerned, and work is currently in progress to develop a computer program to carry out this task.

Finally, we note that as yet no attempts have been made to fit $\nu_2 = 2$ levels to the molecular parameters of the perturbed Hamiltonian (*19*). Work is also in progress to remedy this deficiency.

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