# Improved Analysis of the Experimental Data on the $H_2D^+$ and $D_2H^+$ Absorption Spectra

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An improved analysis of the $\nu_1$ fundamental bands of the molecular ions $H_2D^+$ and $D_2H^+$ has been carried out with two MW frequencies of $H_2D^+$ and combination differences from the $\nu_2$ and $\nu_3$ bands of $H_2D^+$ and $D_2H^+$. It is shown that the previous analysis of the $\nu_1$ bands was poor because of misassignments. The following reassignments are made: for $H_2D^+$, the line 3168.702 $cm^{-1}$ is assigned to $5_{05}$–$4_{04}$; for $D_2H^+$, the line 2990.154 $cm^{-1}$ is assigned to $4_{41}$–$3_{30}$; the assignments of the lines 2899.242 and 2899.362 $cm^{-1}$ are interchanged (this interchange was confirmed independently (S. C. Foster, A. R. W. McKellar, and J. K. G. Watson, *J. Chem. Phys.* **85**, 664, 1986)); the line 2832.859 $cm^{-1}$ is presumably due to the $5_{15}$–$5_{14}$ transition of $H_2D^+$. This reassignment results in a fit that is about five times better than that in the previous model of up to $J^4$ for $H_2D^+$ and up to $J^6$ for $D_2H^+$. A Padé model of a one-dimensional approximation of Watson's Hamiltonian is used in both cases. © 1988 Academic Press, Inc.

## INTRODUCTION

The $H_3^+$ molecular ion plays an important part in the formation of molecules in the interstellar medium (*1*), and the $H_2D^+$ and $D_2H^+$ ions are important in the deuterium fractionation of interstellar molecules. They have permanent dipole moments and, therefore, pure rotational spectra. Some lines of these spectra have been observed in the laboratory (*2–4*) as well as by radio astronomy (*5*). The $H_3^+$ ion belongs to the series of the "simplest" quantum systems: H is the simplest atom, $H_2$ is the simplest diatomic molecule, and $H_3^+$ is the simplest polyatomic molecule. The $H_2D^+$ and $D_2H^+$ molecular ions are the lightest asymmetric top molecules. Thus, a precise analysis of the spectra of these ions is interesting from the viewpoint of both the development of the theory of centrifugal distortion in light molecules and applications in astrophysics and quantum chemistry.

## ANALYSIS

The IR spectra of the $\nu_1$, $\nu_2$, and $\nu_3$ fundamental bands of the $H_2D^+$ and $D_2H^+$ were studied in Refs. (*6–10*). According to the authors of these papers the experimental uncertainty in the determination of the absorption line centers was about $2 \times 10^{-3}$ $cm^{-1}$.

In these investigations experimental data on the line frequencies of rotational and rovibrational spectra of $H_2D^+$ and $D_2H^+$ were analyzed. Thirty-seven frequencies of the $\nu_1$-band transitions of $H_2D^+$ together with two MW rotational frequencies were fitted in Ref. (*8*). The standard deviation in a model of conventional Watson's Hamiltonian (*11*) with terms up to $J^6$ was $2.5 \times 10^{-2}$ $cm^{-1}$:

$$\sigma = \left[\sum_{i=1}^{N}\left(\frac{\nu_{\text{obs.}}^i - \nu_{\text{cal.}}^i}{\sigma_i}\right)^2 \Big/ (N-P)\right]^{1/2}. \tag{1}$$

The fit of 35 line frequencies of the $\nu_1$ band of D$_2$H$^+$ in the same model ($10$) resulted in the standard deviation $\sigma = 4.4 \times 10^{-2}$ cm$^{-1}$. Thus, the accuracy of the calculated frequencies was more than 10 times worse than the experimental uncertainty.

The data on the $\nu_2$ and $\nu_3$ absorption bands of the H$_2$D$^+$ molecular ion were analyzed in Ref. ($6$) and data on the D$_2$H$^+$ ion were analyzed in Ref. ($7$) by means of a one-dimensional approximation of Watson's Hamiltonian ($11$) suggested in Ref. ($12$). As a result of the fitting the standard deviation $\sigma$ was $9 \times 10^{-3}$ cm$^{-1}$ for 73 line frequencies of H$_2$D$^+$ and $26 \times 10^{-3}$ cm$^{-1}$ for 88 line frequencies of D$_2$H$^+$.

We used the method reported in Ref. ($12$) to reanalyze the $\nu_1$ bands of the H$_2$D$^+$ and D$_2$H$^+$ ions and found that by reassigning some frequencies of the bands mentioned above the experimental data could be fitted to an accuracy close to the experimental results.

Combined refitting of 37 line frequencies of the fundamental band $\nu_1$ of H$_2$D$^+$ ($8$), two known MW frequencies ($2$–$4$), and 20 combination differences from the ground state from the $\nu_2$- and $\nu_3$-band data ($6$) was carried out by the following Padé model of a one-dimensional approximation of Watson's Hamiltonian ($12$) including terms up to $J^4$:

$$H = {}^P H_{\text{diag}} + \tfrac{1}{2}\,{}^P H_{\text{offdiag}}(J_x^2 - J_y^2) + \tfrac{1}{2}(J_x^2 - J_y^2)\,{}^P H_{\text{offdiag}};$$

$$^P H_{\text{diag}}^{(4)} = \frac{C_0^2}{C_0 - C_1}; \qquad ^P H_{\text{offdiag}}^{(4)} = \frac{b_0^2}{b_0 - b_1};$$

$$C_0 = \frac{B+C}{2}J^2 + \left(A - \frac{B+C}{2}\right)J_z^2; \qquad b_0 = \frac{B-C}{2};$$

$$C_1 = -\Delta_J J^4 - \Delta_{JK}J^2 J_z^2 - \Delta_K J_z^4; \qquad b_1 = -2(\delta_J J^2 + \delta_K J_z^2). \tag{2}$$

After the reassignment of the 3168.702-cm$^{-1}$ frequency from $5_{14}$–$4_{14}$ to $5_{05}$–$4_{04}$ the standard deviation $\sigma = 9 \times 10^{-3}$ cm$^{-1}$ was obtained for IR data. The differences between the experimental and calculated values of frequencies reported in Ref. ($8$) and in this work are presented in Table I. The MW frequencies and combination differences taken from Ref. ($6$) are given in the first part of Table III together with the differences between the calculated and experimental values. The three combination differences of the ground state obtained by using the 2429.647-cm$^{-1}$ line of the $\nu_3$ band ($6$) differ by about 0.04 cm$^{-1}$ from the ones obtained by using the $\nu_1$- and $\nu_2$-band frequencies ($6$, $8$). Hence, the frequency of this line is probably incorrect by about 0.04 cm$^{-1}$. We did not include these differences in the fit. Molecular constants of H$_2$D$^+$ in both the ground and (100) states are presented in Table IV.

The refit of 34 out of 35 line frequencies of the $\nu_1$ fundamental band of D$_2$H$^+$ from Ref. ($10$) and 20 combination differences on the ground state from Ref. ($7$) was carried out in the Padé model of one-dimensional approximation including terms up to $J^4$ (Eq. (2)) for the ground state and in the Padé model with a diagonal part of the Hamiltonian including terms up to $J^6$,

TABLE I

Results of the $\nu_1$ Band of $H_2D^+$ Analysis (in $cm^{-1}$)

| Transision | | $\nu_{obs.}$ | $(\nu_{obs.} - \nu_{cal.}) \cdot 10^3$ | |
| --- | --- | --- | --- | --- |
| $J'K_a'K_c'$ ← $J''K_a''K_c''$ | | Ref. [8] | This work | Ref. [8] |
| 3 1 3 | 4 1 4 | 2839.387 | 4 | 10 |
| 2 1 1 | 3 1 2 | 2840.962 | 18 | 2 |
| 2 0 2 | 3 0 3 | 2871.897 | 1 | 2 |
| 2 1 2 | 3 1 3 | 2974.811 | -3 | -6 |
| 1 1 0 | 2 1 1 | 2887.370 | -6 | 24 |
| 2 0 2 | 2 2 1 | 2904.657 | -1 | -1 |
| 1 0 1 | 2 0 2 | 2906.523 | -7 | -20 |
| 1 1 1 | 2 1 2 | 2911.635 | -11 | 12 |
| 0 0 0 | 1 0 1 | 2946.802 | -8 | -13 |
| 2 1 2 | 2 1 1 | 2952.940 | 1 | -7 |
| 3 2 2 | 3 2 1 | 2963.513 | 3 | -16 |
| 3 3 1 | 3 3 0 | 2975.064 | -4 | 14 |
| 1 1 1 | 1 1 0 | 2978.045 | 1 | 15 |
| 3 3 0 | 3 3 1 | 2978.492 | 3 | -11 |
| 2 2 1 | 2 2 0 | 2979.987 | -1 | -9 |
| 2 2 0 | 2 2 1 | 2991.162 | 5 | 1 |
| 1 1 0 | 1 1 1 | 3003.276 | 0 | 23 |
| 3 2 1 | 3 2 2 | 3009.123 | 9 | 9 |
| 2 1 1 | 2 1 2 | 3028.263 | 1 | -2 |
| 1 0 1 | 0 0 0 | 3038.177 | 5 | -21 |
| 3 1 2 | 3 1 3 | 3063.006 | -10 | -10 |
| 2 1 2 | 1 1 1 | 3068.845 | 6 | -9 |
| 2 2 1 | 2 0 2 | 3072.190 | -3 | -11 |
| 2 0 2 | 1 0 1 | 3077.611 | 4 | 2 |
| 2 1 1 | 1 1 0 | 3094.671 | 10 | 0 |
| 3 1 3 | 2 1 2 | 3104.207 | 1 | 11 |
| 3 0 3 | 2 0 2 | 3109.645 | -3 | 46 |
| 3 2 2 | 2 2 1 | 3121.202 | -4 | -13 |
| 4 1 4 | 3 1 3 | 3137.007 | 7 | -23 |
| 4 0 4 | 3 0 3 | 3139.197 | 3 | -32 |
| 3 2 1 | 2 2 0 | 3140.044 | 7 | 0 |
| 3 1 2 | 2 1 1 | 3141.131 | -9 | -15 |
| 4 2 3 | 3 2 2 | 3160.971 | -20 | 25 |
| 5 0 5 | 4 0 4 | 3168.702 | -8 | |
| 4 1 3 | 3 1 2 | 3178.973 | -20 | 26 |
| 4 2 2 | 3 2 1 | 3193.963 | -2 | -4 |
| 5 1 4 | 4 1 3 | 3208.187 | 18 | -14 |

$$^P H_{diag}^{(6)} = C_0 + \frac{C_1^2}{C_1 - C_2};$$

$$C_2 = H_J J^6 + H_{JK} J^4 J_z^2 + H_{KJ} J^2 J_z^4 + H_K J_z^6, \tag{3}$$

for the (100) vibrational state. The off-diagonal part for the (100) state was the same as that in Eq. (2). We used a higher order in the diagonal part of the Hamiltonian for the excited state because of higher $J$ and $K$ for the (100) data than for the ground state (see Table II).

TABLE II

Results of the $\nu_1$ Band of D$_2$H$^+$ Analysis (in cm$^{-1}$)

| Transision | | $\nu_{obs.}$ | $(\nu_{obs.} - \nu_{cal.}) \cdot 10^3$ | |
|---|---|---|---|---|
| $J'K_a'K_c' \leftarrow J''K_a''K_c''$ | | Ref. [10] | This work | Ref. [10] |
| 2 0 2 | 3 1 3 | 2637.524 | 8 | 10 |
| 1 0 1 | 2 1 2 | 2661.258 | 20 | 6 |
| 1 1 1 | 2 0 2 | 2683.613 | 0 | -47 |
| 2 0 2 | 2 1 1 | 2701.189 | 12 | 9 |
| 1 1 0 | 1 0 1 | 2759.036 | 1 | 52 |
| 2 1 1 | 2 0 2 | 2769.753 | -10 | 53 |
| 3 2 1 | 3 1 2 | 2777.196 | 2 | -46 |
| 2 2 0 | 2 1 1 | 2779.238 | -1 | 32 |
| 4 2 2 | 4 1 3 | 2782.543 | 0 | 36 |
| 1 1 1 | 0 0 0 | 2785.332 | 0 | -46 |
| 2 0 2 | 1 1 1 | 2788.300 | 11 | 8 |
| 3 1 2 | 3 0 3 | 2788.990 | -11 | -57 |
| 2 2 1 | 2 1 2 | 2802.436 | -1 | 7 |
| 2 1 2 | 1 0 1 | 2810.800 | -6 | -37 |
| 4 1 3 | 4 0 4 | 2815.314 | -1 | 5 |
| 3 2 2 | 3 1 3 | 2815.778 | 5 | -22 |
| 3 0 3 | 2 1 2 | 2820.564 | 2 | 18 |
| 3 1 3 | 2 0 2 | 2832.828 | -14 | 6 |
| 4 0 4 | 3 1 3 | 2849.066 | 1 | -16 |
| 4 1 4 | 3 0 3 | 2854.421 | -11 | 27 |
| 2 2 1 | 1 1 0 | 2854.707 | 3 | 8 |
| 2 2 0 | 1 1 1 | 2866.350 | 1 | 33 |
| 5 0 5 | 4 1 4 | 2874.948 | 9 | -45 |
| 5 1 5 | 4 0 4 | 2876.954 | 0 | 22 |
| 3 2 2 | 2 1 1 | 2879.442 | 6 | -22 |
| 4 2 3 | 3 1 2 | 2899.242 | 6 | |
| 6 0 6 | 5 1 5 | 2899.362 | -2 | |
| 5 2 4 | 4 1 3 | 2915.899 | 0 | -32 |
| 3 2 1 | 2 1 2 | 2918.238 | 2 | -46 |
| 3 3 1 | 2 2 0 | 2924.524 | -3 | -13 |
| 3 3 0 | 2 2 1 | 2928.067 | 0 | 0 |
| 4 3 2 | 3 2 1 | 2951.532 | -10 | 7 |
| 4 3 1 | 3 2 2 | 2968.334 | 7 | -11 |
| 4 4 1 | 3 3 0 | 2990.154 | 2 | |

To obtain an accuracy close to the experimental value, we reassigned the following three transitions: 2990.154 cm$^{-1}$ was reassigned from $4_{40}$–$3_{31}$ to $4_{41}$–$3_{30}$; 2899.242 cm$^{-1}$ was reassigned to $4_{23}$–$3_{12}$, and 2899.362 cm$^{-1}$ was reassigned to $6_{06}$–$5_{15}$. This yielded the standard deviation $\sigma = 7 \times 10^{-3}$ cm$^{-1}$. The results of the analysis for the $\nu_1$ band of D$_2$H$^+$ are given in Table II and for the $\nu_2$ and $\nu_3$ bands combination differences are presented in the second part of Table III. The molecular constants of the (000) and (100) states are given in Table IV. The 2832.859-cm$^{-1}$ transition was excluded from the fit. It may be due to the $5_{15}$–$5_{14}$ transition of the $\nu_1$ band of H$_2$D$^+$. This suggestion can be verified by a test of the dependence of this line's intensity on the H$_2$/D$_2$ ratio in a discharge. The exchange in the assignment of the two lines and exclusion of the 2832.859-cm$^{-1}$ line from the fit were confirmed independently in Ref. (7).

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TABLE III

MW Frequencies (in MHz) and Combination Differences (in $cm^{-1}$) of $H_2D^+$ and $D_2H$
in the Ground State from the $\nu_2$ and $\nu_3$ Bands Data

| Assignment $J'K_a'K_c' \leftarrow J''K_a''K_c''$ | obs. | $(\nu_{obs.} - \nu_{cal.}) \cdot 10^3$ |
|---|---|---|
| $H_2D^+$ | | |
| 2 2 0    2 2 1 | 155 987.185 | -35 |
| 1 1 0    1 1 1 | 372 421.380 | 0 |
| | | |
| 3 0 3    2 2 1 | 32.758 | -4 |
| 2 1 2    1 1 0 | 66.403 | -4 |
| 4 1 4    3 1 2 | 77.520 | 13 |
| 3 1 3    2 1 1 | 78.124 | 0 |
| 2 2 0    2 0 2 | 92.201 | 4 |
| 2 1 1    1 1 1 | 115.904 | -4 |
| 3 2 2    2 2 0 | 130.922 | 1 |
| 2 0 2    0 0 0 | 131.660 | -12 |
| 3 3 0    3 1 2 | 133.670 | -7 |
| 2 2 1    1 0 1 | 172.953 | 4 |
| 3 1 2    2 1 2 | 187.300 | 15 |
| 3 1 3    1 1 1 | 194.028 | 3 |
| 3 0 3    1 0 1 | 205.711 | 0 |
| 3 2 2    2 0 2 | 223.125 | 3 |
| 3 1 2    1 1 0 | 253.711 | 3 |
| 3 3 1    2 1 1 | 282.407 | 8 |
| 3 3 0    2 1 2 | 320.967 | 11 |
| 5 1 4    4 1 4 | 335.094 | -8 |
| 3 3 0    1 1 0 | 387.381 | 4 |
| 3 3 1    1 1 1 | 398.315 | -1 |
| | | |
| $D_2H^+$ | | |
| 3 0 3    2 2 1 | 16.935 | -5 |
| 2 1 2    1 1 0 | 52.271 | 5 |
| 3 1 2    2 1 1 | 63.665 | 2 |
| 4 1 4    3 1 2 | 65.952 | 4 |
| 2 2 0    2 0 2 | 80.346 | 3 |
| 2 1 1    1 1 1 | 87.111 | -1 |
| 3 2 2    2 2 0 | 101.251 | -5 |
| 2 0 2    0 0 0 | 101.719 | 0 |
| 3 1 2    2 1 2 | 141.042 | 0 |
| 2 2 1    1 0 1 | 144.246 | 0 |
| 3 1 3    1 1 1 | 150.775 | 0 |
| 3 0 3    1 0 1 | 161.183 | -4 |
| 3 2 2    2 0 2 | 181.598 | 0 |
| 3 1 2    1 1 0 | 193.314 | 6 |
| 4 1 3    3 1 3 | 199.021 | 1 |
| 4 2 3    3 0 3 | 223.366 | 12 |
| 5 1 4    4 1 4 | 257.547 | 0 |
| 4 1 3    2 1 1 | 262.685 | 2 |
| 4 3 1    3 1 3 | 323.358 | -3 |
| 5 1 4    3 1 2 | 323.492 | -4 |

In Table V we present the calculated rotational levels of the $H_2D^+$ and $D_2H^+$ ions in the ground and (100) states up to $J, K = 6$.

Besides the fit of the $\nu_1$ bands in the models of Eqs. (2) and (3), a fit was made in the model by using a higher order of the perturbation theory, i.e., with terms up to $J^6$ (12 constants both for the ground and excited states). The standard deviations in this case were $2 \times 10^{-3}$ cm$^{-1}$. We do not present the results of this fit because the experimental data analyzed did not include enough levels with high $J$ and $K$ (except the (100) state of $D_2H^+$) to yield "true" values of the $H$ constants. These incorrect constants lead to incorrect energy levels for high rotational quantum numbers ($K > 4$). It is obvious that analysis of the data with higher rotational quantum numbers will require that the model be expanded.

## PREDISSOCIATION SPECTRUM

In conclusion we discuss an additional aspect that has aroused much interest in the study of the spectra of the $H_3^+$ ion and its deuterated species. We are referring to the 27 000 lines of the $H_3^+$ predissociation spectrum and the several thousand lines of its deuterated species in the region 872–1092 cm$^{-1}$ (13), the interpretation of which is very complicated. Carrington and Kennedy (13) suggested that the $H_3^+$ ion be considered a complex of the $H_2$ molecule and the $H^+$ proton and interpreted its spectrum as the splitting of transitions between various rovibrational levels of the $H_2$ molecule due to its interaction with the proton. Their supposition was partially confirmed by computer simulation of a pseudo-low-resolution spectrum of $H_3^+$. However, the calculation and assignment of specific frequencies proved to be impossible in this model (14); hence

TABLE IV

Molecular Constants of $H_2D^+$ and $D_2H^+$ Ions for the Ground (000) and the (100) Vibrational States (in cm$^{-1}$)

| Constant | $H_2D^+$ | | $D_2H^+$ | |
|---|---|---|---|---|
| | (000) | (100) | (000) | (100) |
| $\nu_0$ | | 2992.505(6) | | 2736.941(2) |
| A | 43.4385(18) | 41.6057(28) | 36.19394(34) | 35.47188(35) |
| B | 29.13355(95) | 29.3205(32) | 21.87711(31) | 21.63468(28) |
| C | 16.60138(95) | 16.3854(32) | 13.06462(31) | 12.94104(28) |
| $\Delta_J \cdot 10^3$ | 10.012(12) | 9.8927(38) | 5.847(10) | 6.241(17) |
| $\Delta_{JK} \cdot 10^3$ | 0.17(13) | 1.75(23) | 1.876(31) | −1.49(21) |
| $\Delta_K \cdot 10^2$ | 3.022(14) | 2.523(24) | 1.8688(63) | 3.7747(95) |
| $\delta_J \cdot 10^3$ | 4.0306(62) | 3.889(24) | 2.2696(35) | 2.3235(38) |
| $\delta_K \cdot 10^2$ | 1.9563(36) | 0.241(15) | 1.4218(66) | 1.3441(54) |
| $H_J \cdot 10^6$ | | | | 7.06(23) |
| $H_{JK} \cdot 10^5$ | | | | 6.57(33) |
| $H_{KJ} \cdot 10^4$ | | | | −2.511(71) |
| $H_K \cdot 10^3$ | | | | 1.6044(85) |

### TABLE V

Calculated Rotational Energy Levels of $H_2D^+$ and $D_2H^+$ Ions in the Ground and the (100) Vibrational States (in $cm^{-1}$)

| Level J $K_a K_c$ | $H_2D^+$ (000) | (100) | $D_2H^+$ (000) | (100) |
|---|---|---|---|---|
| 1 0 1 | 45.695 | 45.666 | 34.918 | 34.551 |
| 1 1 1 | 60.023 | 57.985 | 49.250 | 48.390 |
| 1 1 0 | 72.446 | 70.794 | 57.988 | 57.012 |
| 2 0 2 | 131.641 | 130.796 | 101.719 | 100.597 |
| 2 1 2 | 138.846 | 136.357 | 110.255 | 108.783 |
| 2 1 1 | 175.924 | 174.601 | 136.362 | 134.540 |
| 2 2 1 | 218.641 | 211.327 | 179.165 | 175.751 |
| 2 2 0 | 223.844 | 217.294 | 182.061 | 178.658 |
| 3 0 3 | 251.405 | 248.784 | 196.105 | 193.875 |
| 3 1 3 | 254.050 | 250.547 | 200.025 | 197.612 |
| 3 1 2 | 326.158 | 324.557 | 251.296 | 248.165 |
| 3 2 2 | 354.773 | 347.345 | 283.317 | 278.857 |
| 3 2 1 | 376.340 | 371.379 | 296.024 | 291.550 |
| 3 3 1 | 458.337 | 442.384 | 377.137 | 369.647 |
| 3 3 0 | 459.822 | 444.321 | 377.764 | 370.290 |
| 4 0 4 | 402.869 | 398.094 | 315.748 | 312.148 |
| 4 1 4 | 403.672 | 398.544 | 317.245 | 313.596 |
| 4 1 3 | 516.162 | 512.645 | 399.045 | 394.122 |
| 4 2 3 | 531.363 | 523.256 | 419.459 | 413.591 |
| 4 2 2 | 581.526 | 577.800 | 450.698 | 444.647 |
| 4 3 2 | 645.612 | 630.171 | 519.383 | 510.624 |
| 4 3 1 | 654.549 | 641.467 | 523.386 | 514.703 |
| 4 4 1 | 778.679 | 750.636 | 643.435 | 630.974 |
| 4 4 0 | 779.016 | 751.134 | 643.543 | 631.086 |
| 5 0 5 | 586.232 | 579.073 | 460.410 | 455.242 |
| 5 1 5 | 586.451 | 579.172 | 460.922 | 455.761 |
| 5 1 4 | 738.753 | 731.827 | 574.792 | 567.682 |
| 5 2 4 | 745.556 | 735.556 | 585.599 | 578.003 |
| 5 2 3 | 833.302 | 829.355 | 643.205 | 635.035 |
| 5 3 3 | 876.711 | 861.459 | 696.002 | 685.657 |
| 5 3 2 | 904.227 | 894.620 | 709.542 | 699.320 |
| 5 4 2 | 1012.446 | 985.357 | 820.580 | 806.866 |
| 5 4 1 | 1015.142 | 989.284 | 821.480 | 807.794 |
| 5 5 1 | 1177.314 | 1133.988 | 976.540 | 959.853 |
| 5 5 0 | 1177.380 | 1134.099 | 976.556 | 959.870 |
| 6 0 6 | 801.565 | 791.728 | 630.235 | 623.344 |
| 6 1 6 | 801.621 | 791.747 | 630.398 | 623.529 |
| 6 1 5 | 990.977 | 980.368 | 774.945 | 765.509 |
| 6 2 5 | 993.220 | 981.429 | 779.847 | 770.238 |
| 6 2 4 | 1123.612 | 1116.851 | 869.149 | 858.399 |
| 6 3 4 | 1148.124 | 1132.322 | 905.168 | 892.990 |
| 6 3 3 | 1206.268 | 1199.357 | 936.747 | 924.637 |
| 6 4 3 | 1291.575 | 1265.605 | 1032.841 | 1017.713 |
| 6 4 2 | 1302.653 | 1281.116 | 1036.844 | 1021.786 |
| 6 5 2 | 1454.532 | 1412.177 | 1186.797 | 1169.045 |
| 6 5 1 | 1455.187 | 1413.264 | 1186.961 | 1169.412 |
| 6 6 1 | 1650.503 | 1589.083 | 1373.906 | 1356.976 |
| 6 6 0 | 1650.515 | 1589.105 | 1373.908 | 1356.978 |

we had to consider the $H_3^+$ ion as an integral molecule. In using such an approach in the interpretation of the predissociation spectrum one must take into account the centrifugal distortion. For very high rotational quantum numbers, the centrifugal effects predicted by the perturbation theory give absurd results (negative or excessively high positive energy levels and the like). We have demonstrated (*16*) that the method in Ref. (*12*) gives predictions of high $J$ and $K$ levels of light molecules thousands of times more precise than values calculated with the standard polynomial Hamiltonian. So we inserted the constants of $H_3^+$ for the ground and the first excited vibrational states obtained in Ref. (*15*) in the Hamiltonian of Ref. (*12*) having the form

$$H = \int_0^\infty \frac{C_0^2 e^{-t}}{C_0 - C_1 t} dt;$$

$$C_0 = BJ^2 + (C - B)J_z^2; \qquad C_1 = -D_J J^4 - D_{JK} J^2 J_z^2 - D_K J_z^4$$

and calculated the system of energy levels. The accuracy of the predictions of the energy levels is not high enough to allow a specific assignment of the spectrum in Ref. (*13*), but it gives some levels with $J = 25$–$45$ in two previously mentioned vibrational states close to 35 000 cm$^{-1}$ and the transitions between them with $\Delta J = 1$, $\Delta K = 3$, 1 which are in the region 900–1100 cm$^{-1}$. If we suppose the values of the $B$, $C$, and $D_J$, $D_{JK}$, $D_K$ constants of more excited vibrational states are of the same order of magnitude, it can be shown that we can also obtain the levels near the dissociation threshold and the transitions between them in the region 900–1100 cm$^{-1}$. These calculations do not give us specific assignments of the frequencies of Ref. (*13*) but they demonstrate the validity of the approach of Ref. (*12*) in calculating the levels and transitions of $H_3^+$ near the dissociation threshold. We have shown (*16*) that the inclusion of every perturbation term of higher order gives more precise results, contrary to the effect of the polynomial Hamiltonian, which is divergent. Thus, the knowledge of $H$, $L$, and $P$ constants of $H_3^+$ from the analysis of rovibrational bands permits us to interpret the predissociation spectrum of $H_3^+$.

REFERENCES

1. T. OKA, in "Molecular Ions: Spectroscopy, Structure and Chemistry" (T. A. Miller and V. E. Bandybey, Eds.), pp. 73–90, North-Holland, Amsterdam, 1983.
2. M. BOGEY, C. DEMUYNCK, J. L. DESTOMBES, AND B. LEMOINE, *Astron. Astrophys.* **137**, L15–L16 (1984).
3. H. E. WARNER, W. T. CONNER, R. H. PETRMICHL, AND R. C. WOODS, *J. Chem. Phys.* **81**, 2514 (1984).
4. S. SAITO, K. KAWAGNCHI, AND E. HIROTA, *J. Chem. Phys.* **82**, 45–47 (1985).
5. T. G. PHILLIPS, G. A. BLAKE, J. KEENE, R. C. WOODS, AND E. CHURCHWELL, *Astrophys. J. Lett.* **294**, L45–L48 (1985).

6. S. C. FOSTER, A. R. W. MCKELLAR, I. R. PETERKIN, J. K. G. WATSON, F. S. PAN, M. W. CROFTON, R. S. ALTMAN, AND T. OKA, *J. Chem. Phys.* **84,** 91–99 (1986).

7. S. C. FOSTER, A. R. W. MCKELLAR, AND J. K. G. WATSON, *J. Chem. Phys.* **85,** 664–670 (1986).

8. T. AMANO, *J. Opt. Soc. Amer. B* **2,** 790–798 (1985).

9. T. AMANO AND J. K. G. WATSON, *J. Chem. Phys.* **81,** 2869–2871 (1984).

10. K. G. LUBIC AND T. AMANO, *Canad. J. Phys.* **62,** 1886–1888 (1984).

11. J. K. G. WATSON, *J. Chem. Phys.* **46,** 1935–1949 (1967).

12. O. L. POLYANSKY, *J. Mol. Spectrosc.* **112,** 79–87 (1985).

13. A. CARRINGTON AND R. A. KENNEDY, *J. Chem. Phys.* **81,** 91–112 (1984).

14. J. TENNYSON AND B. T. SUTCLIFFE, *Mol. Phys.* **51,** 887–906 (1984).

15. J. K. G. WATSON, S. C. FOSTER, A. R. MCKELLAR, P. BERNATH, T. AMANO, F. S. PAN, M. W. CROFTON, R. C. ALTMAN, AND T. OKA, *Canad. J. Phys.* **62,** 1875–1885 (1984).

16. O. L. POLYANSKY AND N. F. ZOBOV, "Proceedings of the IXth International Conference on High Resolution IR Spectroscopy, Prague, 1986," p. 84.