

Observation and analysis of the ν_2 and ν_3 fundamental bands of the H_2D^+ ion

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(Received 19 August 1985; accepted 4 September 1985)

The observation of the high-resolution absorption spectrum of the H_2D^+ molecular ion in the region 2010–2610 cm^{-1} in discharges through mixtures of H_2 and D_2 gases is reported. Two types of tunable monochromatic sources are employed, either a diode laser (in Ottawa) or a difference-frequency laser system (in Chicago), and the sensitivity is improved by using either discharge modulation or Doppler velocity modulation techniques. A total of 66 new lines of H_2D^+ have been measured and assigned, mostly on the basis of ground-state combination differences, to specific rotational transitions of the ν_2 and ν_3 bands. These data, as well as the two known microwave lines, are fitted by means of two theoretical models, either an effective Hamiltonian model including a Padé representation of a conventional A -reduced centrifugal Hamiltonian for each vibrational level together with Coriolis and higher rotational interactions between ν_2 and ν_3 , or a supermatrix model in which the matrix of the untransformed Hamiltonian is set up in a large vibration-rotation basis and diagonalized directly. In the supermatrix model most of the vibrationally off-diagonal matrix elements are constrained to values derived from Carney's *ab initio* calculations, while the ν_1 parameters are fitted to the observed lines of Amano. Because of the large number of parameters required in the effective Hamiltonian, the less flexible supermatrix model was valuable as a check of the assignments. The results of these fits make it possible to assign seven of the nine lines reported by Shy, Farley, and Wing in 1981. The observed band origins, $\nu_2 = 2205.87 \text{ cm}^{-1}$ and $\nu_3 = 2335.45 \text{ cm}^{-1}$, as well as the rotational constants, are in good agreement with *ab initio* predictions. With the use of one calculated term value to relate the stacks of levels with even and odd values of K''_a , a table of observed term values of the lower rotational levels of the ground state and the ν_2 and ν_3 states is constructed.

I. INTRODUCTION

The H_3^+ molecular ion is of fundamental importance in physics, chemistry, and astronomy. Although there has been considerable interest in this simplest of polyatomic molecules since its discovery¹ in 1912, high-resolution spectra were not available until 1980, when Oka² detected the ν_2 fundamental band of H_3^+ around 4 μm in the infrared, and Shy, Farley, Lamb, and Wing³ detected the same band for D_3^+ around 5.5 μm . A comprehensive analysis of the H_3^+ spectrum has recently been published⁴ and the reader is referred to that paper, and to reviews by Oka,⁵ Herzberg,⁶ and Porter⁷ for further introductory details.

The isotopes of H_3^+ are of significant interest, and in particular H_2D^+ is of key importance because of its presumed role in the deuterium fractionation of interstellar molecules, and its possession of a permanent electric dipole ($\approx 0.6 \text{ D}$) and hence an allowed pure rotational spectrum. Shy *et al.*⁸ observed several lines of the infrared spectrum of H_2D^+ in 1981, but no specific rotational assignments of these transitions were made at that time. In 1984, Amano and Watson⁹ detected and analyzed the ν_1 fundamental band of H_2D^+ around 3.3 μm , and recently Amano¹⁰ has extended these observations. Subsequently, three groups have detected two pure rotational transitions: 1_{10} – 1_{11} near 372 GHz,^{11,12} and 2_{11} – 2_{12} near 156 GHz.¹³ Based on the laboratory data, a possible detection of the 372 GHz line of this species in the giant molecular cloud NGC 2264 has been

reported.¹⁴ Extensive *ab initio* calculations of the structure and vibrational frequencies of H_2D^+ have been made by Carney and Porter,¹⁵ Carney,^{16,17} and Tennyson and Sutcliffe.¹⁸

In the present paper, we report the observation and analysis of the ν_2 and ν_3 fundamental bands of H_2D^+ in the 4–5 μm region. These results were obtained using tunable infrared laser sources to record the absorption spectrum of mixtures of H_2 and D_2 subjected to an electric discharge. The analysis was complicated by a strong Coriolis interaction between ν_2 (2206 cm^{-1}) and ν_3 (2335 cm^{-1}), but the interaction parameters thereby obtained provide valuable additional information. A total of 66 lines from the ν_2 and ν_3 bands have been measured, assigned, and fitted, and an additional 7 (out of nine) of the lines detected by Shy *et al.*⁸ were assigned with some confidence as specific higher- J (>5) transitions of the ν_2 band. The experimental energy levels and molecular parameters arising from our study are in generally good agreement with previous *ab initio* calculations.^{15–18}

II. EXPERIMENTAL DETAILS

Spectra were obtained in Ottawa using a tunable diode laser source in the 2000–2500 cm^{-1} region, and in Chicago using a tunable difference-frequency laser source⁴ in the 2300–2600 cm^{-1} region. The diode laser apparatus has been described previously^{4,19} and only a brief discussion will be given here. It utilizes a commercial laser source spectrom-

eter and laser diodes manufactured by the Laser Analytics Division of Spectra-Physics Inc. H_2D^+ spectral line positions were calibrated relative to nearby known infrared absorption standards with the aid of interference fringes from a temperature-stabilized Ge etalon. During the present work the system was refined by incorporating three infrared detectors and a three-pen chart recorder so that the sample (H_2D^+), reference gas, and etalon fringe spectra were recorded simultaneously. The absorption cell, based on the design of Van den Heuvel and Dymanus,²⁰ consisted of a large copper hollow cathode, and incorporated multiple-traversal mirrors which gave an effective absorption path of 11.2 m in the discharge region. A discharge modulation scheme^{4,19,21} was used to enhance sensitivity and discriminate in favor of ions, and typical peak currents were 0.6 to 0.8 A. Most spectra were recorded with the hollow cathode directly cooled with flowing liquid nitrogen.

The dependence of the relative intensities of H_3^+ , H_2D^+ , and D_2H^+ spectral lines on $\text{H}_2 : \text{D}_2$ mixing ratio was studied by Amano and Watson,⁹ who found a strong preference for deuterium substitution due to the effect of the lowering of zero-point energies and of the missing $J = 0$ level of H_3^+ . Our observations are in general agreement, and indeed the deuterium preference may be even greater in the hollow cathode cell due to a slightly lower effective temperature (we estimate $T_{\text{rot}} \approx T_{\text{trans}} \approx 150$ K in the hollow cathode, com-

pared to ≈ 200 K in the positive column discharge of Refs. 2 and 9, with both cells cooled by liquid nitrogen). Specifically, we found the H_2D^+ spectrum to be maximized by an $\text{H}_2 : \text{D}_2$ partial pressure ratio of around 80:20, whereas D_2H^+ exhibited a much broader maximum centered about a 50:50 ratio. This difference made it relatively easy to distinguish experimentally between the two molecules except in the case of very weak lines. Many of the present measurements were in fact made while simultaneously searching for H_2D^+ and D_2H^+ transitions using an intermediate $\text{H}_2 : \text{D}_2$ ratio of about 70:30. The D_2H^+ ν_2 and ν_3 band results will be reported in a separate paper, while an analysis of ν_1 was recently published by Lubic and Amano.²²

The difference-frequency laser system used for the measurements in the range 2300–2600 cm^{-1} in Chicago is similar to that described earlier in our paper on H_3^+ .⁴ A liquid-nitrogen cooled ac discharge through a gas mixture with $\text{H}_2 : \text{D}_2 = 75:25$ at a total pressure of 800 mTorr was used in the observations of low- J transitions. Later, higher- J lines were measured using a water-cooled cell. The discharge tube is 12 mm i.d. and about 1 m long, and the radiation is passed through it six times unidirectionally. The velocity modulation technique²³ was used to increase the sensitivity of detection.

The observed wave numbers of 66 lines are presented in Table I, together with our assignments, the residuals in the

TABLE I. Observed lines and assignments in the ν_2 and ν_3 bands of H_2D^+ .

	Upper level	Lower level	ν_{obs}^a	Residual $A^{a,b}$	Residual $B^{a,c}$	Intensity ^d
ν_2	6 ₁₅	7 ₁₆	1837.573 ^e	0.003	0.128	0.0000
ν_2	6 ₂₅	7 ₂₆	1837.688 ^e	0.003	0.186	0.0000
ν_2	5 ₀₅	6 ₀₆	1892.541 ^e	0.006	0.310	0.0005
ν_2	5 ₁₅	6 ₁₆	1892.558 ^e	0.001	0.315	0.0015
ν_2	5 ₁₄	6 ₁₅	1895.995 ^e	0.007	-0.193	0.0003
ν_2	5 ₂₄	6 ₂₅	1896.345 ^e	-0.000	-0.043	0.0001
ν_2	4 ₁₃	5 ₁₄	1952.024 ^e	-0.013	-0.268	0.0010
ν_2	3 ₀₃	4 ₀₄	2012.621	0.012	-0.239	0.0045
ν_2	3 ₁₃	4 ₁₄	2013.010	0.007	-0.202	0.0137
ν_2	2 ₁₁	3 ₁₂	2053.211	-0.002	0.082	0.0053
ν_2	2 ₂₁	3 ₂₂	2060.684	0.001	-0.051	0.0017
ν_2	2 ₀₂	3 ₀₃	2066.958	-0.003	-0.160	0.0075
ν_2	2 ₁₂	3 ₁₃	2068.680	-0.008	-0.148	0.0233
ν_2	4 ₁₄	3 ₃₁	2081.851	-0.005	-0.109	0.0000
ν_2	1 ₁₀	2 ₁₁	2102.488	-0.002	0.068	0.0068
ν_3	2 ₂₁	3 ₃₀	2108.633	-0.001	0.129	0.0097
ν_3	2 ₂₀	3 ₃₁	2111.226	0.004	0.076	0.0105
ν_2	1 ₀₁	2 ₀₂	2115.046	0.004	-0.003	0.0074
ν_2	1 ₁₁	2 ₁₂	2119.938	-0.008	-0.052	0.0221
ν_3	2 ₁₁	3 ₂₂	2157.701	0.004	-0.147	0.0042
ν_2	0 ₀₀	1 ₀₁	2160.176	0.007	0.054	0.0043
ν_2	1 ₁₁	1 ₁₀	2186.344	-0.001	-0.018	0.0034
ν_3	1 ₁₀	2 ₂₁	2190.664	0.008	-0.097	0.0123
ν_2	2 ₂₀	2 ₂₁	2208.417	0.003	0.076	0.0032
ν_2	1 ₁₀	1 ₁₁	2218.393	0.002	0.101	0.0189
ν_3	2 ₀₂	3 ₁₃	2223.706	-0.002	-0.135	0.0266
ν_2	3 ₂₁	3 ₂₂	2225.501	0.002	0.183	0.0016
ν_3	2 ₁₂	3 ₀₃	2239.637	0.001	0.077	0.0085
ν_2	2 ₁₁	2 ₁₂	2240.512	-0.001	0.121	0.0119
ν_3	2 ₂₁	3 ₁₂	2242.303	-0.005	0.112	0.0037
ν_3	1 ₀₁	2 ₁₂	2245.109	-0.005	-0.120	0.0523
ν_2	1 ₀₁	0 ₀₀	2246.697	-0.002	0.065	0.0018
ν_3	3 ₂₁	3 ₃₀	2257.495	0.005	0.105	0.0082

TABLE I (continued).

	Upper level	Lower level	ν_{obs}^a	Residual $A^{a,b}$	Residual $B^{a,c}$	Intensity ^d
ν_3	4 ₀₄	4 ₁₃	2261.176	-0.012	-0.025	0.0058
ν_3	3 ₁₃	3 ₂₂	2263.807	0.002	0.102	0.0034
ν_3	1 ₁₁	2 ₀₂	2271.135	0.002	0.055	0.0112
ν_3	2 ₁₂	2 ₂₁	2272.395	-0.013	0.102	0.0071
ν_3	0 ₀₀	1 ₁₁	2275.403	-0.003	-0.101	0.0749
ν_3	4 ₁₃	4 ₂₂	2279.085	0.018	0.119	0.0027
ν_2	2 ₂₁	2 ₀₂	2283.810	0.003	-0.013	0.0033
ν_3	3 ₀₃	3 ₁₂	2284.565	0.004	-0.035	0.0233
ν_2	4 ₁₃	4 ₁₄	2287.118	0.008	-0.288	0.0037
ν_3	2 ₁₁	2 ₂₀	2288.623	-0.003	-0.133	0.0150
ν_2	5 ₀₅	4 ₀₄	2290.658	0.003	-0.137	0.0002
ν_3	2 ₀₂	2 ₁₁	2301.830	0.003	-0.073	0.0686
ν_3	1 ₀₁	1 ₁₀	2311.512	-0.001	-0.090	0.1138
ν_3	2 ₁₁	2 ₀₂	2380.824	0.002	-0.112	0.0206
ν_2	2 ₂₀	1 ₀₁	2381.367	0.000	0.147	0.0025
ν_3	2 ₂₀	2 ₁₁	2393.633	-0.007	0.100	0.0388
ν_3	1 ₁₁	0 ₀₀	2402.795	0.005	0.132	0.0413
ν_3	2 ₀₂	1 ₁₁	2417.734	0.005	-0.041	0.0660
ν_3	2 ₂₁	2 ₁₂	2429.647	0.039	0.194	0.0250
ν_3	2 ₁₂	1 ₀₁	2445.348	-0.010	0.177	0.0456
ν_3	3 ₁₂	2 ₂₁	2445.606	-0.011	-0.111	0.0032
ν_2	3 ₂₁	2 ₀₂	2448.627	0.002	0.220	0.0010
ν_3	3 ₃₁	3 ₂₂	2466.041	0.002	-0.175	0.0020
ν_3	3 ₀₃	2 ₁₂	2471.865	0.003	0.002	0.0810
ν_3	3 ₁₃	2 ₀₂	2486.932	0.001	0.139	0.0376
ν_3	4 ₂₃	4 ₁₄	2490.782	-0.020	-0.064	0.0040
ν_3	2 ₂₁	1 ₁₀	2496.014	0.007	0.189	0.1070
ν_3	4 ₁₃	3 ₂₂	2505.693	-0.017	0.066	0.0031
ν_3	2 ₂₀	1 ₁₁	2509.541	-0.000	0.136	0.0922
ν_2	3 ₃₁	2 ₁₂	2512.598	-0.002	-0.120	0.0092
ν_3	4 ₀₄	3 ₁₃	2523.271	0.004	-0.008	0.0541
ν_3	4 ₁₄	3 ₀₃	2523.953	-0.001	0.021	0.0074
ν_3	3 ₂₂	2 ₁₁	2534.328	0.003	0.195	0.0579
ν_2	4 ₂₂	3 ₀₃	2537.200	-0.001	-0.090	0.0148
ν_3	4 ₂₃	3 ₁₂	2568.302	0.018	0.042	0.0262
ν_3	5 ₀₅	4 ₁₄	2571.585	-0.003	-0.162	0.0245
ν_3	5 ₁₅	4 ₀₄	2572.755	-0.001	-0.178	0.0079
ν_3	3 ₂₁	2 ₁₂	2578.462	-0.002	0.123	0.0334
ν_3	3 ₃₁	2 ₂₀	2596.960	-0.008	-0.164	0.0177
ν_3	3 ₃₀	2 ₂₁	2602.146	0.006	-0.161	0.0182

^a Units: cm⁻¹.^b Residual (observed-calculated) from effective Hamiltonian fit.^c Residual (observed-calculated) from supermatrix fit.^d Line strength (in D²) multiplied by lower-state Boltzmann factor at 200 K.^e Data from Shy, Farley, and Wing (Ref. 8).

two different fits described in Sec. III, and the calculated relative intensities at 200 K. Also included in Table I are assignments of seven of the nine lines measured by Shy, Farley, and Wing.⁸

III. THEORETICAL MODELS

The (ν_2 , ν_3) spectrum of H₂D⁺ is essentially a many-line spectrum, with no obvious branches or regularities, and we have found it valuable to use two different theoretical approaches in order to have a crosscheck on the analysis and line assignments. The first approach employs a conventional effective vibration-rotation Hamiltonian within the near-degenerate (ν_2 , ν_3) diad, while the second approach employs a larger vibration-rotation supermatrix in which most of the off-diagonal elements are constrained at values derived from *ab initio* calculations.¹⁷ In the effective Hamiltonian the vi-

bration-rotation matrix elements between the ν_2 and ν_3 states are included explicitly, but the effects of other off-diagonal matrix elements are represented in the usual way by centrifugal distortion terms for each vibrational state. The advantages of the effective Hamiltonian approach are that it is easier and cheaper to implement because the matrices are relatively small and additional terms are readily added. However, for a light molecule such as H₂D⁺ a rather large number of centrifugal terms is required. The advantage of the supermatrix approach is that the Hamiltonian contains no terms higher than quadratic in the total angular momentum, but the matrices are in general large and expensive to diagonalize. In this approach the vibration-rotation matrix elements must be parametrized so that they can be extrapolated to higher vibrational states, but it is relatively easy to incorporate constraints based on *ab initio* values of vibration-rotation matrix elements.¹⁷

A. Effective Hamiltonian model

In the effective Hamiltonian approach, the rotational levels of the ground vibrational state of H₂D⁺ are represented by a *I*' A-reduced asymmetric rotor Hamiltonian,²⁴ with one important modification, namely the use of Padé-type expressions to represent the sextic and higher centrifugal distortion terms. This was adopted following the notable success⁴ achieved by applying Padé expressions to the fitting of the ν_2 bands of H₃⁺ and D₃⁺. The specific approach followed here is based on that recently formulated by Polyansky,²⁵ which has the merit of treating the centrifugal distortion in a way that can be easily related to the conventional power series approach,²⁴ using distortion parameters whose limiting values are the same as the conventional series coefficients.

The specific form of the rotational Hamiltonian used here for a vibrational level ν is as follows:

$$H_\nu = (H_{\text{diag}})_\nu + (H_{\text{off-diag}})_\nu, \quad (1)$$

$$(H_{\text{diag}})_\nu = H_{2\nu} + H_{4\nu}^2 / (H_{4\nu} - H_{6\nu}), \quad (2)$$

$$(H_{\text{off-diag}})_\nu = [J_b^2 - J_c^2, \{h_{2\nu} + h_{4\nu}^2 / (h_{4\nu} - h_{6\nu})\}]_+,$$

$$H_{2\nu} = A_\nu J_a^2 + \frac{1}{2}(B_\nu + C_\nu)(J^2 - J_a^2),$$

$$H_{4\nu} = -\Delta_\nu^{KK} J_a^4 - \Delta_\nu^{JK} J^2 J_a^2 - \Delta_\nu^{JJ} J^4, \quad (3)$$

$$H_{6\nu} = \Phi_\nu^{KKK} J_a^6 + \Phi_\nu^{JKK} J^2 J_a^4 + \Phi_\nu^{JJK} J^4 J_a^2 + \Phi_\nu^{JJJ} J^6,$$

$$h_{2\nu} = \frac{1}{2}(B_\nu - C_\nu),$$

$$h_{4\nu} = -\delta_\nu^K J_a^2 - \delta_\nu^J J^2, \quad (4)$$

$$h_{6\nu} = \phi_\nu^{KK} J_a^4 + \phi_\nu^{JK} J^2 J_a^2 + \phi_\nu^{JJ} J^4.$$

It can easily be seen that in the limit of small centrifugal distortion ($H_{6\nu} \ll H_{4\nu}$, $h_{6\nu} \ll h_{4\nu}$), these expressions reduce to the usual A-reduced form²⁴ for an asymmetric rotor in a prolate symmetric rotor basis.

For the near-degenerate (ν_2 , ν_3) diad, we use diagonal blocks specified by Eqs. (1)–(4) and add an off-diagonal block to describe the Coriolis and higher-order rotational interactions between the fundamentals. The major interaction between ν_2 and ν_3 is due to the Coriolis term \tilde{H}_{21} , in the notation of Aliev and Watson,²⁶ and we also include centrifugal corrections to it of the type \tilde{H}_{23} ,

$$\begin{aligned} \tilde{H}_{21} + \tilde{H}_{23} &= (q_2 p_3 - q_3 p_2) \\ &\times \{ -\xi_{23} J_c + \eta_{23}^K J_a J_c J_a + \eta_{23}^J J^2 J_c \}. \end{aligned} \quad (5)$$

In the harmonic approximation ξ_{23} is given by

$$\xi_{23} = (\omega_2 + \omega_3) C_e \xi_{23}^c / (\omega_2 \omega_3)^{1/2}, \quad (6)$$

but we implicitly allow for anharmonic deviations from this (\tilde{H}_{41} terms) by treating ξ_{23} as an adjustable parameter. The centrifugal corrections η_{23}^K and η_{23}^J are similar to the constants η_i^K and η_i^J of symmetric top molecules.²⁷ The fundamentals also interact through a term of the type \tilde{H}_{22} , which can be regarded as an off-diagonal vibration-rotation α correction.

$$(\tilde{H}_{22})_{\text{off-diag}} = -\alpha_{23}^{ab} (q_2 q_3 + p_2 p_3) (J_a J_b + J_b J_a). \quad (7)$$

The combined matrix elements of Eqs. (5) and (7) with prolate symmetric-rotor rotational functions are

$$\begin{aligned} &\langle \nu_2, J, k_a | \tilde{H}_{21} + \tilde{H}_{22} + \tilde{H}_{23} | \nu_3, J, k_a \pm 1 \rangle \\ &= \frac{1}{2} \{ \pm [\xi_{23} - \eta_{23}^K k_a (k_a \pm 1) - \eta_{23}^J J(J+1)] \\ &\quad - \alpha_{23}^{ab} (2k_a \pm 1) \} \\ &\quad \times [J(J+1) - k_a (k_a \pm 1)]^{1/2}. \end{aligned} \quad (8)$$

The various coefficients here include the effects of perturbations by other vibrational states, particularly ν_1 , but in the effective Hamiltonian procedure they are treated as empirical parameters whose values are determined by an optimum fit to the spectrum. The lower-order coefficients ξ_{23} and α_{23}^{ab} are, however, equivalent to F_{32} and $-D_{32}/2$, respectively, of Carney¹⁷ (see Sec. III regarding the sign of the Coriolis term) or to G_{23} and $-F_{23}$, respectively, of Tennyson and Sutcliffe,¹⁸ so that there exist *ab initio* estimates of these parameters.

B. Vibration-rotation supermatrix model

In the supermatrix calculations it is assumed that the basic vibration-rotation Hamiltonian²⁶ has been transformed by a *J*-independent contact transformation which diagonalizes the pure vibrational energy. This produces an effective Hamiltonian that can be expressed as a power series in the vibrational coordinates q_k and momenta p_k , but which contains no terms higher than quadratic in the total angular momentum. The specific form chosen is

$$\begin{aligned} H &= \sum_k \nu_k v_k + \sum_k x_{kk} v_k (v_k - 1) + \sum_{k < l} x_{kl} v_k v_l \\ &+ \sum_\alpha B^{\alpha\alpha} J_a^2 + B^{ab} (J_a J_b + J_b J_a) \\ &- 2 J_c \{ C_e \xi_{13}^c (\omega_3 q_1 p_3 - \omega_1 q_3 p_1) / (\omega_1 \omega_3)^{1/2} \\ &+ C_e \xi_{23}^c (\omega_3 q_2 p_3 - \omega_2 q_3 p_2) / (\omega_2 \omega_3)^{1/2} \}, \end{aligned} \quad (9)$$

where v_k is an abbreviation for

$$v_k = \frac{1}{2}(q_k^2 + p_k^2 - 1) \quad (10)$$

and the rotational tensor components are given by

$$\begin{aligned} B^{\alpha\alpha} &= B_0^{\alpha\alpha} + \sum_{k=1,2} \rho_k^{\alpha\alpha} q_k \\ &- \sum_{k=1,2,3} \alpha_{kk}^{\alpha\alpha} (q_k^2 - 1/2) - 2\alpha_{12}^{\alpha\alpha} q_1 q_2, \end{aligned} \quad (11)$$

$$B^{ab} = \rho_3^{ab} q_3 - 2 \sum_{k=1,2} \alpha_{k3}^{ab} q_k q_3.$$

In the final line of Eq. (9) the harmonic frequencies ω_k are calculated from the other parameters according to

$$\omega_k = \nu_k - 2x_{kk} - \frac{1}{2} \sum_{k' \neq l} x_{kl}. \quad (12)$$

To calculate the vibration-rotation energy levels from this Hamiltonian it is necessary to use a moderate to large vibrational basis together with a complete set of rotational functions for each *J*. Since the three vibrational frequencies

are comparable in magnitude, it was decided to base the criterion for inclusion in the vibrational basis set purely on the value of the total vibrational quantum number

$$V_{\text{tot}} = \sum_k V_k. \quad (13)$$

For an accuracy of $\sim 0.1 \text{ cm}^{-1}$ in the lower- J rotational levels of the $V_k = 1$ states a value of $V_{\text{tot}} = 2$ was adequate, but the final calculations were performed with $V_{\text{tot}} = 3$. To facilitate the use of this program for the symmetrical isotopes H₃⁺ and D₃⁺, a Wang oblate rotational basis was used. In order that the matrix elements of the Hamiltonian should be all real, the phase of the vibrational functions were chosen to make the matrix elements of q_1 , q_2 , and p_3 real and positive, so that

$$\begin{aligned} \langle V_k \pm 1 | q_k | V_k \rangle &= \mp i \langle V_k \pm 1 | p_k | V_k \rangle \\ &= \frac{1}{2}(2V_k + 1 \pm 1)^{1/2}, \quad k = 1, 2, \end{aligned} \quad (14)$$

$$\begin{aligned} \langle V_3 \pm 1 | p_3 | V_3 \rangle &= \pm i \langle V_3 \pm 1 | q_3 | V_3 \rangle \\ &= \frac{1}{2}(2V_3 + 1 \pm 1)^{1/2}. \end{aligned} \quad (15)$$

Initial values for the parameters in this Hamiltonian can be derived from the *ab initio* calculations of Carney and Porter.¹⁵⁻¹⁷ The vibrational parameters ν_k and x_{kl} were determined from the vibrational levels with $V_{\text{tot}} < 2$ in Ref. 15, while the rotational and Coriolis parameters in Eqs. (9) and (11) were determined from the matrix elements with $V_{\text{tot}} < 1$ given by Carney.¹⁷ In this comparison it was assumed that Carney's matrix elements could be equated with the matrix elements of Eq. (9) evaluated in a basis in which Eq. (14) is valid for all three modes. Once the values of the parameters were obtained in this way, the basis (14) and (15) was used to calculate the matrix elements for the present calculations.

Some inconsistencies with calculations by the effective Hamiltonian method eventually led to the suspicion that the signs of the Coriolis matrix elements F_{nm} of Carney are all incorrect, and this was confirmed by a calculation of these matrix elements in the harmonic approximation. For example, the product of matrix elements $D_{13}F_{32}C_{21}$ (in Carney's notation) is independent of phase choices, and is -751 cm^{-3} from Carney's table, whereas the harmonic calculation gave $+987 \text{ cm}^{-3}$. By changing the sign of all the F_{nm} elements, a consistent set of phases is obtained.

The matrix elements of the Hamiltonian (9) were calculated by first setting up the matrix elements of each vibrational and rotational operator separately and then combining them together as a sum of products. For $V_{\text{tot}} < 3$ and $J < 6$ the maximum dimension of the matrices is 73. In view of the slowness of diagonalizing a number of such large matrices, it is not feasible to vary as many parameters in fitting the spectrum as in the effective Hamiltonian method. It was therefore decided as a general rule to adjust only the V-diagonal coefficients ν_k , $B_0^{\alpha\alpha}$, and $\alpha_{kk}^{\alpha\alpha}$, and to constrain the V-off-diagonal coefficients to the values derived from Carney's matrix elements¹⁷ with the sign change discussed above. The only exception to this rule was the coefficient α_{23}^{ab} between the near-degenerate levels ν_2 and ν_3 . Adjustment of the coefficient $C_e \zeta_{23}^c$ was attempted, but was found to give moderately strong correlations with α_{22}^{cc} and α_{33}^{cc} . The resulting

slow convergence of the least-squares fit made the calculations very slow, and it was decided to constrain this coefficient to its *ab initio* value.

IV. ANALYSIS

A preliminary (ν_2, ν_3) spectrum of H₂D⁺ was calculated with the vibration-rotation supermatrix program of Sec. II B, using the *ab initio* vibration-rotation matrix elements of Ref. 17 and *ab initio* electric dipole transition moments derived from Refs. 15 and 28. This gave a good general picture of the structure of the spectrum, but at this stage there were some minor errors in the supermatrix program and also the phase inconsistency in the matrix elements of Ref. 15 (see Sec. III B) was not appreciated. For these reasons there were difficulties in making detailed line assignments, and it was decided initially to accept only those assignments that were supported by ground-state combination differences.^{9,10} In fact, many of the measurements in Table I were made in searches for lines separated by known differences from previously measured and tentatively assigned lines. Eventually most of the previously observed ground-state differences^{9,10} were confirmed and a number of additional new ones were established. Wherever possible the assignments in Table I are supported in this way.

The observation of a known ground-state difference between lines does not uniquely identify the common upper level of the lines, particularly when one is dealing with overlapping and interacting bands, and therefore the assignments of the upper levels are based on calculated spectra. These assignments can then be included in a least-squares refinement of the parameters in either of the theoretical models of Sec. III, and new predictions and assignments become possible. The main intention in the supermatrix approach is to make comparatively small adjustments in a few of the parameters, so that the calculations should remain physically reasonable, possibly at the expense of a poorer fit of the line positions. In the effective Hamiltonian approach a larger number of parameters is varied and a more precise fit is obtained, but for such more flexible models there is a greater danger of misassignments being accepted and then being difficult to diagnose, essentially because particular parameters may be determined purely by the energy of particular misassigned levels. The two parallel approaches should therefore act as checks on each other, and the final set of assignments in Table I is supported by both models.

Table I also contains assignments of seven out of nine lines observed in the region 1837–1952 cm^{-1} by Shy *et al.*⁸ In view of the fact that the effective temperature of their ion source is rather high, the two remaining lines may have higher J values or may belong to one of the hot bands. Our assignments of four of these lines agree with those of Tennyson and Sutcliffe,^{18(b)} but we have changed the K_c assignments of the $P(7)$ doublet of ν_2 at 1837 cm^{-1} from 6–7 to 5–6. Their assignments would give a doublet about 9 cm^{-1} lower with a smaller splitting and a 3:1 intensity ratio in the opposite sense. The other change is in the assignment of the 1952 cm^{-1} line, for which Tennyson and Sutcliffe suggested either a $P(5)$ or a $Q(5)$ line, but we have chosen a different component of $P(5)$.

The relative intensities in Table I are theoretical values calculated for a rotational temperature of 200 K from the eigenvectors of the supermatrix model, using the dipole moment and derivatives for this isotope,

$$(\mu_a)_e = 0.607 \text{ D}, \quad (\partial\mu_a/\partial q_1)_e = 0.119 \text{ D},$$

$$(\partial\mu_a/\partial q_2)_e = 0.112 \text{ D}, \quad (\partial\mu_b/\partial q_3)_e = 0.275 \text{ D}, \quad (16)$$

obtained from the dipole moment function of Ref. 28, and allowing for the 3:1 ratio of proton spin statistics. We have not included observed intensities because reliable estimates are difficult to make when, as here, the lines are mostly measured individually over a period of months, and the mixing ratios and experimental conditions are adjusted frequently in order to identify the carrier of each line. Qualitatively, the observed relative intensities are similar to those calculated, and minor differences may be due to a somewhat lower rotational temperature or to slight variations in the experimental conditions.

V. RESULTS

The results of our assignments can be presented in terms of a table of rotational term values of the three vibrational states involved. Ground-state combination differences allow us to build up the level stacks with $K_a K_c = ee, eo, oe, oo$ separately, while the two observed microwave lines allow us to relate ee to eo and oe to oo . To complete the level scheme, we have related $K_a = e$ to $K_a = o$ by calculating the separation $1_{11} - 0_{00}$ from effective rotational constants that were fitted to the ground-state differences. With these ground-state term values established, the upper-state term values are obtained by simple addition to the line wave numbers. The results are presented in Table II. For the ground state, we find on average that the *ab initio* rotational term values of Carney¹⁶ are 0.26% higher, while those of Tennyson and Sutcliffe^{18(a)} are 0.13% lower. These discrepancies are similar to those found for the ground state of H₃⁺,⁴ although the Carney deviations are here somewhat smaller than the 0.34% found for H₃⁺. The rotational energies calculated by Tennyson and Sutcliffe^{18(b)} for levels of the ν_2 states are within 0.7% of the observed values in Table II, but the deviations are somewhat variable for different levels.²⁹

The ground state rotational transition $3_{30} - 3_{31}$ is of some interest because it lies in a convenient region of the microwave spectrum and might be observable from astronomical sources.³⁰ From ground state combination differences and the observed microwave line $1_{10} - 1_{11}$, the $3_{30} - 3_{31}$ line is calculated to be at $1.4885 \text{ cm}^{-1} = 44624 \text{ MHz}$ with an estimated uncertainty of $\pm 100 \text{ MHz}$. This is significantly lower than the unidentified line U45.379 observed at Nobeyama Radio Observatory.³¹

In the determination of molecular constants the line wave numbers for the ν_2 and ν_3 bands, together with the two known microwave frequencies¹¹⁻¹³ with a relative weight of 100, were fitted with the effective Hamiltonian of Sec. III A. Altogether 75 lines were included in the fit and 39 parameters were adjusted, giving the values presented in Table III. The standard deviation of the fit of the infrared lines was 0.0093 cm^{-1} . The closest comparable theoretical values are

TABLE II. Observed rotational term values of H₂D⁺.^a

Level	Ground state	ν_2 state	ν_3 state
0 ₀₀	0	(2205.880)	(2335.438)
1 ₀₁	45.703	40.819	48.534
1 ₁₁	60.034	52.922	67.355
1 ₁₀	72.457	72.548	73.881
2 ₀₂	131.655	112.493	142.332
2 ₁₂	138.864	116.867	155.613
2 ₁₁	175.940	173.497	177.043
2 ₂₁	218.655	209.585	233.031
2 ₂₀	223.859	221.192	234.136
3 ₀₃	251.415		275.292
3 ₁₃	254.066	210.816	283.149
3 ₁₂	326.165		328.823
3 ₂₂	354.780		374.830
3 ₂₁	376.344	374.402	381.890
3 ₃₁	458.348	445.582	485.382
3 ₃₀	459.835		485.363
4 ₀₄			441.900
4 ₁₄	403.685	334.319	439.930
4 ₁₃	516.161	484.922	525.035
4 ₂₃			559.029
4 ₂₂	581.388	582.736	
5 ₀₅			639.832
5 ₁₄	738.778		

^a Units: cm^{-1} . The level 1_{11} of the ground state is calculated from effective constants in order to relate the stacks with even and odd values of K'' .

those of Tennyson and Sutcliffe^{18(b), 29} and these are included in Table III. The agreement is generally reasonable, the most important differences being in the set of constants (C_2, C_3, ξ_{23}), for which the strong correlations mean that small differences in the data can produce quite large differences in the constants.

In the supermatrix model of Sec. III B the above data set was supplemented with the lines of the ν_1 band,^{9,10} and a total of 111 lines were fitted with 16 adjustable parameters. As the standard deviation of 0.13 cm^{-1} is clearly limited by the present theory, the data were not weighted. The resulting constants are reported in Table IV, where they are compared with the values derived from Carney's *ab initio* matrix elements.¹⁷ Clearly the agreement is good, and with the correct phases the Carney matrix elements would have provided a rather accurate prediction of the structure of the spectrum.

The optimum values of the band origins ν_2 and ν_3 obtained here are compared in Table V with a number of theoretical estimates. There is good agreement of the calculations among themselves and with the experimental values, except that the original *ab initio* values of Tennyson and Sutcliffe^{18(a)} seem unusually low. The recent calculations of Carney and Adler-Golden³⁷ are particularly close to the observed values.

Apart from zero-point vibrational effects and small terms from the breakdown of the Born-Oppenheimer approximation, the A_0 rotational constant of H₂D⁺ should be the same as B_0 of H₃⁺. The observed value⁴ of the latter is $B_0 = 43.565 \text{ cm}^{-1}$, slightly larger than A_0 of H₂D⁺ from either of the two fitting models employed here. The two models give slightly different values of the ground-state rotational constants A_0, B_0, C_0 . Part of the difference can be explained by considering the second-order effects of the $\rho_k^{\alpha\beta}$

TABLE IV. Parameters from the supermatrix fit of the ν_1 , ν_2 , and ν_3 bands of H₂D⁺.^a

Parameter	Observed ^b	Correlation ^c	<i>Ab initio</i> ^d
A_0	43.3874(81)	1.8	43.146
B_0	29.0597(56)	1.5	28.864
C_0	16.6621(39)	2.0	16.563
ν_1	2992.413(40)	3.4	2999.71
α_1^{aa}	1.7771(109)	2.2	1.747
α_1^{bb}	-0.1674(76)	2.9	-0.119
α_1^{cc}	0.4224(46)	2.2	0.395
ν_2	2205.799(45)	2.8	2203.11
α_2^{aa}	1.2197(163)	3.5	1.188
α_2^{bb}	-1.2934(96)	3.6	-1.324
α_2^{cc}	0.4238(59)	4.5	0.403
ν_3	2335.494(47)	4.2	2328.51
α_3^{aa}	-2.7089(122)	3.4	-2.612
α_3^{bb}	1.2949(100)	4.1	1.189
α_3^{cc}	0.9895(78)	5.5	0.762
α_{23}^{ab}	1.9854(129)	2.1	1.753

^aThe following parameters are constrained at values derived from Carney and Porter (Refs. 15 and 17): $x_{11} = -56.0$, $x_{22} = -46.0$, $x_{33} = -26.5$, $x_{12} = -136.0$, $x_{13} = -83.0$, $x_{23} = -42.0$, $\rho_1^{aa} = -11.8709$, $\rho_1^{bb} = -2.9083$, $\rho_1^{cc} = -2.9628$, $\rho_2^{aa} = -7.0781$, $\rho_2^{bb} = 8.0398$, $\rho_2^{cc} = 1.6794$, $\rho_3^{ab} = 8.1742$, $\alpha_{12}^{aa} = 1.2285$, $\alpha_{12}^{bb} = -1.5575$, $\alpha_{12}^{cc} = -0.0575$, $\alpha_{13}^{ab} = -0.1215$, $C_e \xi_{13}^c = -6.1959$, $C_e \xi_{23}^c = -13.6789$ (all in cm⁻¹).

^bObserved value in cm⁻¹ with standard deviation on last digit in parentheses.

^cThe correlation of each parameter is the diagonal element of the reciprocal of the matrix of correlation coefficients (Ref. 4).

^d*Ab initio* values are derived from Carney (Ref. 17).

terms of Eq. (11), which produce the $\tau_{\alpha\beta\gamma\delta}$ centrifugal constants³⁸ according to

$$\tau_{\alpha\beta\gamma\delta} = -2 \sum_k \rho_k^{\alpha\beta} \rho_k^{\gamma\delta} / \nu_k. \quad (17)$$

The rearrangement³⁹ and reduction⁴⁰ of the centrifugal terms to the *A*-reduced form of Eqs. (1)–(4) produce the following differences in the rotational constants:

$$\begin{aligned} A_0^{(A)} - A_0^{(sm)} &= -\tau_{abab}/2 + 16R_6, \\ B_0^{(A)} - B_0^{(sm)} &= -\tau_{abab}/2 - 16(A - C)R_6/(B - C), \end{aligned} \quad (18)$$

TABLE V. Theoretical and observed values of ν_2 and ν_3 of H₂D⁺.

Potential surface	Vibrational calculation	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)
Carney and Porter, 1974 ^a	Carney and Porter, 1977 ^b	2203	2329
Schinke, Dupuis, and Lester, 1980 ^c	Tennyson and Sutcliffe, 1984 ^d	2184.0	2309.7
Burton <i>et al.</i> , 1985 ^e	Tennyson and Sutcliffe, 1985 ^f (fit A)	2196.1	2321.3
Burton <i>et al.</i> , 1985 ^e	Tennyson and Sutcliffe, 1985 ^f (fit B)	2202.7	2331.8
Burton, <i>et al.</i> , 1985 ^e	Jensen, Špirko, and Bunker, 1985 ^g	2200.1	2325.2
Meyer, Botschwina and Burton, 1985 ^h	Meyer, Botschwina, and Burton, 1985 ^h	2204.4	2332.8
Dykstra and Swope, 1979 ⁱ	Carney and Adler-Golden, 1985 ^j	2207	2336
Observed ^k		2205.87	2335.45

^aReference 28.

^bReference 15.

^cReference 32.

^dReference 18(a).

^eReference 33.

^fReference 18(c).

^gReference 34.

^hReference 35.

ⁱReference 36.

^jReference 37.

^kPresent work.

$$C_0^{(A)} - C_0^{(sm)} = 3\tau_{abab}/4 + 16(A - B)R_6/(B - C),$$

with

$$R_6 = (\tau_{bbbb} + \tau_{cccc} - 2\tau_{bbcc} - 4\tau_{bccc})/64. \quad (19)$$

The calculated differences (18) are, respectively 0.0195, 0.0485, and -0.0537 cm⁻¹, while the observed differences from the fits are 0.0787, 0.0782, and -0.0594 cm⁻¹. Clearly, this contribution provides only a partial explanation of the differences. In general, the delta centrifugal constants from the effective Hamiltonian fit are larger than the values calculated from the formulas⁴⁰ relating them to the taus (17), and apparently there are compensating changes in the principal rotational constants.

In the upper states the two fits give different values for the three constants (C_2 , C_3 , ξ_{23}) but this is largely a result of the strong correlation between these constants. In the effective Hamiltonian fit these three constants are all varied, but in the supermatrix model this correlation is constrained by maintaining the Coriolis interaction at its *ab initio* value.¹⁷

The data for the rotational structure of the three fundamental bands of H₂D⁺ make it possible to obtain a first estimate of the equilibrium structure of H₃⁺. The equilibrium rotational constants determined from the supermatrix fit are

$$A_e = 43.531, \quad B_e = 28.977, \quad C_e = 17.580 \text{ cm}^{-1}. \quad (20)$$

These give the inertial defect $\Delta_e = I_e^c - I_e^a - I_e^b = -0.0101 \text{ u}\text{\AA}^2$, compared to the zero-point value $\Delta_0 = +0.0431 \text{ u}\text{\AA}^2$. The appreciable negative value of Δ_e is probably due to the neglect of γ terms in the extrapolation of the rotational constants. The structural parameters derived from A_e and B_e are

$$r_e(\text{HH}) = 0.8766 \text{ \AA}, \quad r_e(\text{HD}) = 0.8773 \text{ \AA},$$

$$\theta_e(\text{HDH}) = 59^\circ 57',$$

and the deviation from exact equilateral geometry is probably due to the neglect of the γ terms. The *ab initio* estimates of r_e are generally somewhat shorter, close to $1.650a_0 = 0.8731 \text{ \AA}$.

ACKNOWLEDGMENTS

We are grateful to T. Amano for numerous discussions, and to B. T. Sutcliffe, J. Tennyson, P. R. Bunker, P. Botschwina, and G. D. Carney for information in advance of publication. The research at the University of Chicago is supported by NSF Grant No. 84-08316.

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