

High resolution, rotation, vibration spectra of D₂O in the region of ν_1 and ν_3 bands*

V D GUPTA

Department of Physics, Lucknow University, Lucknow 226 007, India

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Abstract. The infrared spectrum of D₂O from 2400 to 3000 cm⁻¹ has been analysed at a resolution better than 0.02 cm⁻¹. It was recorded at the Fourier transform spectrometer of the Kitt Peak National Observatory, Tucson. Ground state constants of the reduced Watson-Hamiltonian, ground state energies and transition for the ν_1 and ν_3 bands are reported. The effect of strong Coriolis resonances on the spectra is discussed.

Keywords. Fourier transform; Coriolis resonance; Wilson-Hamiltonian; high resolution; vibration spectra.

1. Introduction

Recently several studies have been reported on the rotational spectrum, electric dipole measurements and ground state constants of D₂O molecule (Dyke and Muentor 1973; Clough *et al* 1973; Posener and Strandberg 1954; Benedict *et al* 1970; Jen *et al* 1953; Steenbeckeliers *et al* 1970; Bellet *et al* 1970; Steenbeckeliers and Bellet 1973; Brittain 1972). However, to the best of the authors' knowledge no work on vibration-rotation spectrum has been published in the region of ν_1 and ν_3 bands since that of Benedict *et al* (Benedict *et al* 1953, 1956) (3.55 to 4.17 μ). Some heterodyne measurements (Werehesky *et al* 1978) and an analysis of the constants (Lin and Shaw 1977) in the ν_2 region have been reported (Lin and Shaw 1977; Williamson 1969). The ν_1 , ν_3 and ν_2 bands correspond to the symmetrical stretch, antisymmetrical stretch and angle-bend respectively. In the 2400 to 2500 cm⁻¹ region, there is also a considerable overlap between the ν_1 and $2\nu_2$ bands. ν_3 is an A type band whereas ν_1 and $2\nu_2$ are of type B (vibrational symmetries are just opposite).

The basic data on rotation and rotation-vibration constants on D₂O are important because, when combined with the results on HDO and H₂O, they provide a very rigorous test of the assumption that the molecular dimensions and potential function remain unchanged by isotopic substitution.

The data reported by Benedict *et al* (1953, 1956) were taken on grating spectrometers with PbS and PbTe detectors and resolution varying from 0.25 to 0.3 cm⁻¹. In the present investigation the spectrum was recorded on the Fourier transform spectrometer of the McMath solar telescope at the Kitt Peak National Observatory,

*Work done at the Jet Propulsion Laboratory, Division of Stratospheric and Planetary Research California Institute of Technology, Pasadena, Ca (U.S.A.)

Tucson. The resolution after apodization was better than 0.02 cm^{-1} . InSb detectors were used. The main purpose of the present paper is to report high resolution data in the region of ν_1 and ν_3 bands and accurate values of the rotational constants and centrifugal distortions which yield precise ground state energies which are consistent with microwave as well as infrared transitions.

For light asymmetric rotors, such as D_2O , centrifugal distortion effects are extremely important in the interpretation of the observed spectra. The reduced Hamiltonian including distortion effects through P^{10} for a prolate asymmetric rotor has the form

$$H = H_r + H_d^{(4)} + H_d^{(6)} + H_d^{(8)} + H_d^{(10)},$$

$$\text{where } Hr = \frac{1}{2} (B + C) P^2 + [A - \frac{1}{2} (B + C)] (P_z^2 - b_p P_-^2),$$

$$H_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 \\ - \delta_K (P_z^2 P_-^2 + P_-^2 P_z^2),$$

$$H_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{JK} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2 \\ + 2h_{JK} P^2 (P_z^2 P_-^2 + P_-^2 P_z^2) + h_K (P_z^4 P_-^2 + P_-^2 P_z^4),$$

$$H_d^{(8)} = L_J P^8 + L_{JK} P^6 P_z^2 + L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P^8 \\ + 2l_J P^6 P_-^2 + l_{JK} P^4 (P_z^2 P_-^2 + P_-^2 P_z^2) + l_{KJ} P^2 (P_z^4 P_-^2 \\ + P_-^2 P_z^4) + l_K (P_z^6 P_-^2 + P_-^2 P_z^6),$$

$$H_d^{(10)} = P_J P^{10} + P_{JK} P^8 P_z^2 + P_{JK} P^6 P_z^4 + P_{KJ} P^4 P_z^6 \\ + P_{KKJ} P^2 P_z^8 + P_K P_z^{(10)} + P_{2J} P^8 P_-^2 + P_{JK} P^6 (P_x^2 P_-^2 \\ + P_-^2 P_x^2) + P_{JK} P^4 (P_z^4 P_-^2 + P_-^2 P_z^4) + P_{KKJ} P^2 (P_z^6 P_-^2 \\ + P_-^2 P_z^6) + P_K (P_z^8 P_-^2 + P_-^2 P_z^8),$$

where Δ_J , etc are the quartic distortion coefficients and H_J , etc are sextic distortion coefficients. Similarly coefficients in terms of degree eight and ten in the angular momentum are defined.

$$b_p = \frac{C-B}{2A-B-C}$$

is Wang's asymmetry parameter

$$P^2 = P_x^2 + P_y^2 + P_z^2 \text{ and } P_-^2 = P_x^2 - P_y^2.$$

The rotational constants in the reduced Hamiltonian (A, B, C) are related to the effective rotational constants (A_k, B_k, C_k) defined by Kivelson and Wilson (1953) as

$$A = A_k + 16 R_6,$$

$$B = B_k - 16 R_6 (A_k - C_k) / (B_k - C_k),$$

$$C = C_k + 16 R_6 (A_k - B_k) / (B_k - C_k),$$

where R_6 is quartic distortion constant. The Watson's reduced Hamiltonian contains $(2n+1)$ terms of degree $2n$, among which $(n+1)$ are purely diagonal (denoted by capital letters) in the usual representation while others are purely off-diagonal of ranks -2 and $+2$ (denoted by small letters).

D_2O is a light molecule and hence the distortion effects are very important. It becomes necessary, therefore, to include some terms of degree eight and ten in the angular momentum to obtain a representative fit of the observed spectrum. It has been shown (Steenbeckeliers *et al* 1970) that the diagonal and off-diagonal terms are of equal importance for small K_a while for large K_a the diagonal terms are the leading ones. It may be mentioned at this stage that these coefficients except the sextic and quartic constants must be regarded as empirical constants in the sense that they have not as yet been theoretically related to the vibrational potential constants. The quartic and sextic ones have been related to the quadratic and cubic force constants. The ground state constants were obtained by a simultaneous fit of the microwave (statistical weight 10^5) and infra-red transition. In general the statistical weight of each level involved is taken inversely proportional to the square of the confidence interval. A nonlinear least fit was carried out. The overall standard deviation between observed and calculated line position is 0.04 cm^{-1} .

The ground state levels and rotational energies reported in table 1 are an improvement over those of (Benedict *et al* 1953, 1956) and Steenbeckeliers and Bellet (1973). The agreement between ground state and the experimental data is much better (for

Table 1a. Constants of D_2O molecule symmetry C_{2v}

| Band | Vibrational symmetry | Rotational symmetry | Band centre (cm^{-1}) |
|----------|----------------------|---------------------|----------------------------------|
| ν_1 | A_1 | B | 2672.0811 |
| ν_2 | A_1 | B | 1178.374* |
| ν_3 | B_1 | A | 2787.7182 |
| $2\nu_2$ | B_1 | B | 2336.8392 |

$$\kappa = -0.5408$$

*(Williamson 1969)

Table 1b. Ground state Watson-constants* For D₂O

| Rotational constants | | |
|-------------------------------------|---|-------------|
| A = 15.41970 | B = 7.27265 | C = 4.84538 |
| Quartic constants | | |
| $\Delta_K = 9.24565 \times 10^{-3}$ | $\Delta_{JK} = -1.53587 \times 10^{-3}$ | |
| $\Delta_J = 3.09608 \times 10^{-4}$ | $\delta_K = 3.65799 \times 10^{-4}$ | |
| | $\delta_J = 1.22103 \times 10^{-4}$ | |
| Sextic constants | | |
| $H_K = 1.85339 \times 10^{-5}$ | $H_{KJ} = -2.80223 \times 10^{-6}$ | |
| $H_{JK} = -2.67578 \times 10^{-7}$ | $H_J = 5.92043 \times 10^{-8}$ | |
| $h_K = 3.94517 \times 10^{-6}$ | $h_{JK} = 9.48093 \times 10^{-8}$ | |
| | $h_J = 2.46848 \times 10^{-8}$ | |
| Octic constants | | |
| $L_K = -5.34657 \times 10^{-8}$ | $L_{KKJ} = 1.957585 \times 10^{-8}$ | |
| $L_{JK} = -5.64416 \times 10^{-9}$ | $l_K = -3.419023 \times 10^{-8}$ | |

*All constants are given in units of cm⁻¹.Table 2. Energy Levels for (000), (100) and (001) bands of D₂O

| J | K _a | K _c | (000) | (100) | (001) | J | K _a | K _c | (000) | (100) | (001) |
|---|----------------|----------------|----------|-----------|-----------|---|----------------|----------------|----------|-----------|-----------|
| 1 | 0 | 1 | 12.1163 | 2683.6053 | 2799.7582 | 1 | 1 | 0 | 22.6837 | 2694.0106 | 2809.8423 |
| 1 | 1 | 1 | 20.2589 | 2691.6061 | 2807.3934 | 2 | 2 | 2 | 35.8775 | 2707.0524 | 2823.3303 |
| 2 | 1 | 1 | 49.3379 | 2720.3287 | 2836.3699 | 2 | 1 | 2 | 42.0692 | 2713.1208 | 2829.0299 |
| 2 | 2 | 0 | 74.1408 | 2744.7099 | 2859.6982 | 2 | 2 | 1 | 73.6754 | 2744.2451 | 2859.1941 |
| 3 | 0 | 3 | 70.4467 | 2741.1542 | 2857.5516 | 3 | 1 | 2 | 88.9688 | 2759.4561 | 2875.7807 |
| 3 | 1 | 3 | 74.5063 | 2745.1158 | 2861.1849 | 3 | 2 | 1 | 112.2492 | 2782.3318 | 2897.7076 |
| 3 | 2 | 2 | 110.0326 | 2780.1209 | 2895.3386 | 3 | 3 | 0 | 156.6614 | 2826.0048 | 2939.5517 |
| 3 | 3 | 1 | 156.6040 | 2825.9465 | 2939.4855 | 4 | 0 | 4 | 114.9863 | 2785.0770 | 2901.5796 |
| 4 | 1 | 3 | 141.0834 | 2810.9007 | 2927.5330 | 4 | 1 | 4 | 117.3123 | 2787.3330 | 2903.5895 |
| 4 | 2 | 2 | 164.1736 | 2833.6034 | 2949.5199 | 4 | 2 | 3 | 158.1052 | 2827.5594 | 2943.1000 |
| 4 | 3 | 1 | 206.2741 | 2874.9513 | 2989.0177 | 4 | 3 | 2 | 205.8811 | 2874.5596 | 2988.5728 |
| 4 | 4 | 0 | 269.3803 | 2937.0367 | 3048.6277 | 4 | 4 | 1 | 269.3744 | 2937.0367 | 3048.6234 |
| 5 | 0 | 5 | 169.0388 | 2838.3745 | 2955.0090 | 5 | 1 | 4 | 204.9335 | 2873.9133 | 2990.7814 |
| 5 | 1 | 5 | 170.2436 | 2839.5364 | 2955.9962 | 5 | 2 | 3 | 229.9865 | 2898.5882 | 3015.1296 |
| 5 | 2 | 4 | 217.5837 | 2886.2420 | 3002.1346 | 5 | 3 | 2 | 269.0065 | 2936.8612 | 3051.6263 |
| 5 | 3 | 3 | 267.5278 | 2935.3545 | 3049.9544 | 5 | 4 | 1 | 331.1216 | 2997.8930 | 3110.2794 |
| 5 | 4 | 2 | 331.0699 | 2997.8927 | 3110.2159 | 5 | 5 | 0 | 411.5432 | 3077.9971 | 3186.2220 |
| 5 | 5 | 1 | 411.5426 | 3077.2272 | 3186.2184 | 6 | 0 | 6 | 232.5225 | 2900.9694 | 3017.8545 |
| 6 | 1 | 5 | 279.5607 | 2947.5381 | 3064.4598 | 6 | 1 | 6 | 233.1067 | 2901.5287 | 3018.2179 |
| 6 | 2 | 4 | 309.2582 | 2976.8415 | 3094.0261 | 6 | 2 | 5 | 288.0922 | 2956.1821 | 3072.0619 |
| 6 | 3 | 3 | 345.4417 | 3012.3003 | 3127.9741 | 6 | 3 | 4 | 341.3860 | 3008.1314 | 3123.4513 |
| 6 | 4 | 2 | 405.5290 | 3071.2520 | 3184.6203 | 6 | 4 | 3 | 405.2809 | 3071.2044 | 3184.2802 |
| 6 | 5 | 1 | 485.5985 | 3149.8673 | 3260.6922 | 6 | 5 | 2 | 485.5926 | 3149.8682 | 3260.6868 |
| 6 | 6 | 0 | 582.4117 | 3244.8733 | 3351.6497 | 6 | 6 | 1 | 582.4117 | 3244.8733 | 3351.6497 |
| 7 | 0 | 7 | 305.4959 | 2972.9229 | 3089.2650 | 7 | 1 | 6 | 364.0433 | 3030.8596 | 3147.7307 |
| 7 | 1 | 7 | 305.7679 | 2973.1802 | 3090.1579 | 7 | 2 | 5 | 401.2543 | 3067.6061 | 3185.3915 |
| 7 | 2 | 6 | 369.2649 | 3035.8833 | 3152.5052 | 7 | 3 | 4 | 436.0534 | 3101.7497 | 3218.4796 |
| 7 | 3 | 5 | 427.1962 | 3093.5457 | 3208.7714 | 7 | 4 | 3 | 492.8773 | 3157.3885 | 3271.8169 |
| 7 | 4 | 4 | 492.0194 | 3156.9221 | 3270.8080 | 7 | 5 | 2 | 572.1621 | 3235.0757 | 3347.5491 |
| 7 | 5 | 3 | 572.1279 | 3235.0827 | 3347.5109 | 7 | 6 | 1 | 668.8487 | 3329.4801 | 3344.3836 |
| 7 | 6 | 2 | 668.8481 | 3329.4556 | 3444.3836 | 7 | 7 | 0 | 781.1696 | 3434.9243 | 3544.1620 |
| 7 | 7 | 1 | 781.1696 | 3434.9243 | 3544.1620 | 8 | 0 | 8 | 388.0195 | 3054.2922 | 3171.2849 |
| 8 | 1 | 7 | 457.8200 | 3123.3316 | 3240.2206 | 8 | 1 | 8 | 388.1431 | 3054.4076 | 3172.6786 |
| 8 | 2 | 6 | 505.0399 | 3169.0023 | 3288.2090 | 8 | 2 | 7 | 460.7643 | 3126.1416 | 3243.1518 |
| 8 | 3 | 5 | 540.8728 | 3205.1895 | 3323.0493 | 8 | 3 | 6 | 524.6066 | 3189.2560 | 3305.5392 |
| 8 | 4 | 4 | 593.5834 | 3256.7176 | 3372.4248 | 8 | 4 | 5 | 591.2165 | 3254.8801 | 3369.6966 |

Table 2. (contd.)

| J | K_a | K_c | (000) | (100) | (001) | J | K_a | K_c | (000) | (100) | (001) |
|----|-------|-------|-----------|-----------|-----------|----|-------|-------|-----------|-----------|-----------|
| 8 | 5 | 3 | 671-3337 | 3332-7451 | 3446-8800 | 8 | 5 | 4 | 671-1934 | 3332-7500 | 3446-7255 |
| 8 | 6 | 2 | 767-7141 | 3426-3879 | 3544-0161 | 8 | 6 | 3 | 767-7099 | 3426-4209 | 3544-0161 |
| 8 | 7 | 1 | 880-0359 | 3531-2272 | 3641-3809 | 8 | 7 | 2 | 880-0358 | 3531-2272 | 3641-3809 |
| 8 | 8 | 0 | 1006-9199 | 3663-5723 | 3762-9135 | 8 | 8 | 1 | 1006-9199 | 3663-5723 | 3762-9135 |
| 9 | 0 | 9 | 480-1255 | 3145-1103 | 3262-4790 | 9 | 1 | 8 | 560-7511 | 3224-8259 | 3341-8329 |
| 9 | 1 | 9 | 480-1806 | 3145-1615 | 3262-4043 | 9 | 2 | 7 | 619-5523 | 3283-2976 | 3401-3288 |
| 9 | 2 | 8 | 562-3151 | 3226-3048 | 3343-8513 | 9 | 3 | 6 | 659-4063 | 3322-0076 | 3441-0625 |
| 9 | 3 | 7 | 633-2143 | 3296-3779 | 3413-3505 | 9 | 4 | 5 | 708-1660 | 3369-7388 | 3486-9179 |
| 9 | 4 | 6 | 702-7020 | 3364-9129 | 3480-7480 | 9 | 5 | 4 | 783-2688 | 3443-7345 | 3558-8318 |
| 9 | 5 | 5 | 782-8096 | 3442-9549 | 3558-3302 | 9 | 6 | 3 | 879-0419 | 3535-7267 | 3655-6804 |
| 9 | 6 | 4 | 879-0221 | 3535-8021 | 3655-6804 | 9 | 7 | 2 | 991-2687 | 3640-1089 | 3750-8591 |
| 9 | 7 | 3 | 991-2682 | 3640-1089 | 3750-8591 | 9 | 8 | 1 | 1118-2563 | 3772-4400 | 3873-3289 |
| 9 | 8 | 2 | 1118-2563 | 3772-4400 | 3873-3289 | 10 | 0 | 10 | 581-8226 | 3245-3815 | 3363-0365 |
| 10 | 1 | 9 | 672-9153 | 3335-4957 | 3452-6356 | 10 | 1 | 10 | 581-8473 | 3245-4143 | 3363-0352 |
| 10 | 2 | 8 | 743-7929 | 3407-0998 | 3523-8024 | 10 | 2 | 9 | 673-7135 | 3336-1751 | 3456-3790 |
| 10 | 3 | 7 | 790-8066 | 3452-5294 | 3571-5686 | 10 | 3 | 8 | 752-6074 | 3414-1637 | 3531-8405 |
| 10 | 4 | 6 | 837-0449 | 3496-8137 | 3615-6410 | 10 | 4 | 7 | 826-1971 | 3487-8677 | 3603-6508 |
| 10 | 5 | 5 | 908-2144 | 3567-9838 | 3683-6405 | 10 | 5 | 6 | 906-9495 | 3563-3027 | 3682-2937 |
| 10 | 6 | 4 | 1002-8797 | 3657-4772 | 3779-4856 | 10 | 6 | 5 | 1002-8056 | 3658-2883 | 3779-4856 |
| 10 | 7 | 3 | 1114-8689 | 3761-4356 | 3872-5981 | 10 | 7 | 4 | 1114-8664 | 3761-4356 | 3782-5981 |
| 10 | 8 | 2 | 1241-9266 | 3893-7847 | 3996-1350 | 10 | 8 | 3 | 1241-9266 | 3893-7847 | 3996-1350 |
| 11 | 0 | 11 | 693-1079 | 3355-1346 | 3473-1230 | 11 | 1 | 10 | 794-4235 | 3455-4206 | 3572-7099 |
| 11 | 1 | 11 | 925-1201 | 3355-1304 | 3473-1272 | 11 | 2 | 9 | 877-1033 | 3539-6072 | 3655-1272 |
| 11 | 2 | 10 | 794-8205 | 3455-6325 | 3572-6304 | 11 | 3 | 8 | 934-0291 | 3589-1136 | 3713-4339 |
| 11 | 3 | 9 | 882-4011 | 3540-9543 | 3660-8506 | 11 | 4 | 7 | 980-2477 | 3637-0596 | 3758-4899 |
| 11 | 4 | 8 | 961-3321 | 3622-6609 | 3738-0672 | 11 | 5 | 6 | 1046-5266 | 3704-5360 | 3821-6937 |
| 11 | 5 | 7 | 1043-5039 | 3702-3749 | 3818-5090 | 11 | 6 | 5 | 1139-2507 | 3791-6770 | 3915-6370 |
| 11 | 6 | 6 | 1139-0571 | 3793-3211 | 3915-6370 | 11 | 7 | 4 | 1250-8268 | 3897-9838 | 4005-9138 |
| 11 | 7 | 5 | 1250-8161 | 3897-9838 | 4005-9138 | 11 | 8 | 3 | 1377-8385 | 4026-4827 | 4128-8750 |
| 11 | 8 | 4 | 1377-8385 | 4026-4827 | 4128-8750 | 12 | 0 | 12 | 813-9718 | 3474-6672 | 1592-6771 |
| 12 | 1 | 11 | 925-3533 | 3584-3589 | 3702-1482 | 12 | 1 | 12 | 813-9766 | 3474-2906 | 3592-6752 |
| 12 | 2 | 10 | 1019-2599 | 3681-4282 | 3795-2454 | 12 | 2 | 11 | 925-5477 | 3584-5444 | 3702-1397 |
| 12 | 3 | 9 | 1087-9532 | 3745-8682 | 3865-4710 | 12 | 3 | 10 | 1022-2802 | 3678-5526 | 3401-9583 |
| 12 | 4 | 8 | 1137-2755 | 3789-9825 | 3914-8262 | 12 | 4 | 9 | 1107-7031 | 3764-6135 | 3883-6572 |
| 12 | 5 | 7 | 1198-6723 | 3852-3653 | 3973-4482 | 12 | 5 | 8 | 1192-2979 | 3847-1168 | 3966-8062 |
| 12 | 6 | 6 | 1288-4144 | 3936-6971 | 4064-3482 | 12 | 6 | 7 | 1287-7164 | 1941-6838 | 4064-3482 |
| 12 | 7 | 5 | 1399-1214 | 4044-0052 | 4152-8856 | 12 | 7 | 6 | 1399-1214 | 4044-0052 | 4152-8856 |
| 12 | 8 | 4 | 1526-0199 | 4319-8921 | 4277-8870 | 12 | 8 | 5 | 1526-0199 | 4182-8660 | 4277-8870 |
| 13 | 0 | 13 | 944-3960 | 3602-8604 | 3721-6898 | 13 | 1 | 12 | 1065-7707 | 3722-7985 | 3840-9452 |
| 13 | 1 | 13 | 944-3982 | 3602-8923 | 3721-7174 | 13 | 2 | 11 | 1170-3670 | 3626-3460 | 3944-2693 |
| 13 | 2 | 12 | 1065-8359 | 3723-3282 | 3840-9580 | 13 | 3 | 10 | 1251-5556 | | 4026-6541 |
| 13 | 3 | 11 | 1171-9928 | | 3944-0358 | 13 | 4 | 9 | 1307-3033 | | 4083-6530 |
| 13 | 4 | 10 | 1264-8783 | | 4040-3158 | 13 | 5 | 8 | 1365-0272 | | 4139-3018 |
| 13 | 5 | 9 | 1352-9816 | | 4126-9429 | 13 | 6 | 7 | 1450-3420 | | 4226-7773 |
| 13 | 6 | 8 | 1448-8491 | | 4226-7773 | 14 | 0 | 14 | 1084-3643 | 3740-9780 | 3860-1400 |
| 14 | 1 | 13 | 1215-6307 | | 3989-0716 | 14 | 1 | 14 | 1084-3653 | 3740-9008 | 3860-1427 |
| 14 | 2 | 12 | 1330-4731 | | 4102-3874 | 14 | 2 | 13 | 1215-6443 | | 3989-0659 |
| 14 | 3 | 11 | 1423-9655 | | | 14 | 3 | 12 | 1331-3592 | | |
| 14 | 4 | 10 | 1489-1376 | | | 14 | 4 | 11 | 1432-4290 | | |
| 14 | 5 | 9 | 1545-5990 | | | 14 | 5 | 10 | 1525-3773 | | |
| 14 | 6 | 8 | 1625-6326 | | | 14 | 6 | 9 | 1622-3012 | | |
| 15 | 0 | 15 | 1233-8571 | 3887-7971 | 4008-0091 | 15 | 1 | 14 | 1374-9441 | 4027-7192 | 4146-6016 |
| 15 | 1 | 15 | 1233-8576 | 3888-3057 | 4008-0091 | 15 | 2 | 13 | 1499-8386 | | |
| 15 | 2 | 14 | 1374-9461 | | 4148-8865 | 15 | 3 | 12 | 1604-9356 | | |
| 15 | 3 | 13 | 1500-2660 | | | 16 | 0 | 16 | 1392-8355 | | 4165-2683 |
| 15 | 0 | 17 | 1561-2916 | | 4331-9948 | 18 | 0 | 18 | 1738-9072 | | 4508-5375 |
| 19 | 0 | 19 | 1926-4338 | | 4693-9409 | 20 | 0 | 20 | 2122-7887 | | |
| 16 | 1 | 16 | 1392-7947 | | 4166-4404 | 17 | 1 | 17 | 1561-2604 | | 4332-2045 |
| 16 | 1 | 15 | 1543-7206 | | 4315-0019 | 16 | 2 | 15 | 1543-7065 | | 4315-5523 |

I.R. within 0.01 cm^{-1}). The constants given by Lin and Shaw (1977) did not yield very satisfactory results. Since these authors have not reported the ground states or the transition levels and the maximum value of J , it is difficult to comment on these results. Our own calculation with their constants yielded ground states in reasonably good agreement with the experimental data upto $J=8$ and $K=4$ but not beyond it.

An attempt was made to fit first the constants for the ν_1 and ν_3 modes separately by dropping the levels which were affected by resonances and later to carry out a simultaneous fit of the two bands by introducing Coriolis interaction constants. Since the ν_1 band also interacts with the $2\nu_2$ band, any attempt to fit ν_1 and ν_3 levels in the absence of $2\nu_2$ levels proved unsuccessful. The interaction between the (100) and (001) states perturbs not only the levels shown in figure 1 but several other neighbouring levels in the sub band. An accurate evaluation of these perturbations is important in the mechanism proposed for D_2O laser emission lines (Benedict *et al* 1969) and will be discussed in a separate publication.

2. Analysis of the spectrum

D_2O is a prolate top having $\kappa = -0.5408$. It is slightly less asymmetric than H_2O ($\kappa = -0.4362$). The spectra have the same general features except that the lines are more closely spaced in D_2O . Since the symmetry axis is the b axis, the ν_3 is an A type

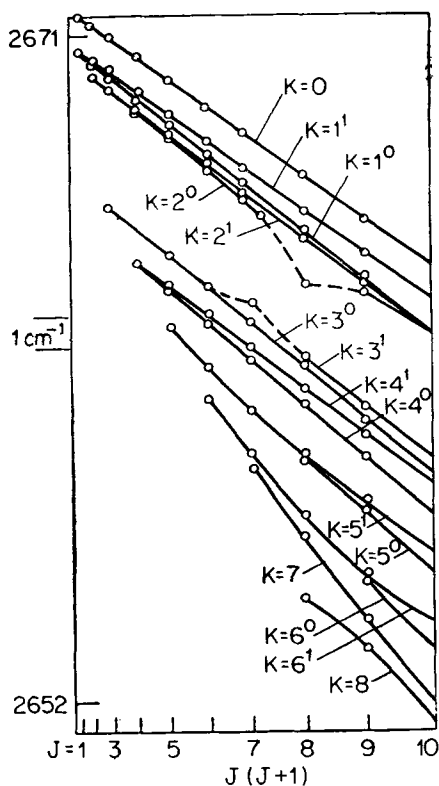


Figure 1. Plot of ΔE versus $J(J+1)$ for ν_1 band

whereas ν_1 and ν_2 are of type *B*. Both in H_2O and D_2O , the weights depend upon the parity of the rotational level designated by $\tau=K_a-K_c$ (the odd: even ratio being 3:1 for H_2O and 1:2 for D_2O .) Due to this, the transitions originating from even K_a in the ground state are stronger than those of adjacent odd K_a sub-bands. The confirmed assignments are listed in asymmetric top notation according to upper and lower J , K_a , K_c and band codes. The band centres listed in table 1 are derived by adding the ground state energies to the transition energy to 000 level.

As reported by all the investigators, it is extremely difficult to obtain the spectrum of D_2O without some contamination from HDO because of the exchange between D_2O and H_2O adsorbed on the walls of the absorption cell. In the 3.7μ region, most of the HDO absorption arises from the O-D stretching fundamental. The lines of HDO, D_2O and H_2O would however, be separately identified by their relative intensity in spectra obtained with different relative proportions of these species. The spectra of D_2O were obtained at vapour pressures of 8, 3 and 1 Torr with a 25 cm cell and at 11.2 Torr with a 1.5 m long cell. All the spectra were analysed and the averages of these measured positions were used in the analysis. Because of the wide variation in the line intensities and blending of neighbouring lines, not all the lines at different pressures were used in obtaining line positions. They were also calibrated and corrected against the standard methane lines reported by Terrago *et al* (1975) with a resolution of 0.005 cm^{-1} .

Initial assignments of the bands were greatly assisted by the work of Benedict *et al* (1953, 1956). The *Q* branches in *A* type bands have a bunched or gathered structure and can be easily recognised. They also locate the band origin. The *B* type bands are relatively weaker but can be assigned with the help of ground-state combination differences. Occasionally due to intensity borrowing through resonances, forbidden lines were needed to confirm assignments. The Loomis-wood diagram also aided in the location of sub-bands and assignments. The ν_3 fundamental is the strongest band and has its band centre at $2787.7182 \text{ cm}^{-1}$ whereas ν_1 which is weaker by a factor of 5 has at $2672.0811 \text{ cm}^{-1}$. Much of the *Q* and *P* branches in $2 \nu_2$ (band centre $2336.8392 \text{ cm}^{-1}$) are hidden by the atmospheric CO_2 absorption.

For an electric dipole transition the selection rules (besides $J=0$, ± 1) are

$$ee \leftrightarrow oo \quad \text{or} \quad eo \leftrightarrow oe \quad \text{for } B \text{ type band } (\nu_1)$$

$$(\Delta K_a = \pm 1),$$

and $ee \leftrightarrow eo \quad \text{or} \quad oo \leftrightarrow oe \quad \text{for } A \text{ type band } (\nu_3)$

$$(\Delta K_a = 0, \Delta K_c = \pm 1).$$

The assignments reported here are believed to be certain giving all the levels upto $J=17$ for $K=0$ and 1 and upto $J=12$ for higher K value. An effective check on the assignments is made by plotting each observed upper state level versus $J(J+1)$ for each K_a . However, the effects of centrifugal distortion on such plots are minimised, if instead a plot is made of ΔE versus $J(J+1)$ where ΔE is the difference between observed upper state energies and calculated ground state energies with the same rotational quantum numbers. Such plots for the ν_1 and ν_3 bands are shown in figures 1 and 2.

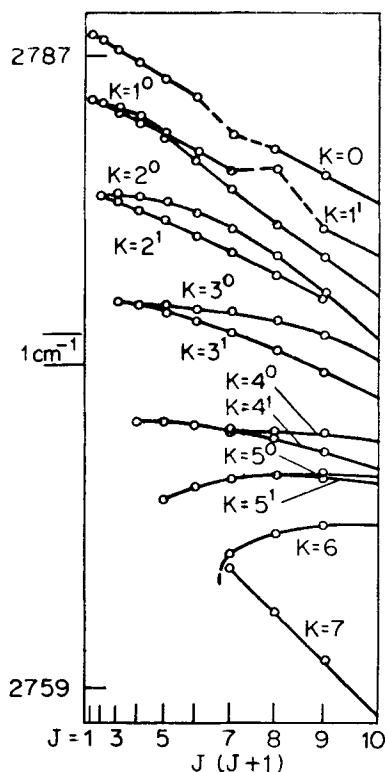


Figure 2. Plot of ΔE versus $J(J+1)$ for ν_3 band

For unperturbed sub-bands, the graphs for different K_a would consist of a set of parallel straight lines whose slope is the difference between the upper and lower states $(B+C)/2$, assuming the subtraction of the ground state energy removes the $[J(J+1)]^{1/2}$ dependence due to centrifugal distortion. Plots of this kind are very helpful in the identification of levels and sub-bands which strongly interact either through Coriolis coupling or Fermi resonance. Such levels show deviations from regular sequences. These exceptions can be accounted for in as much as they occur when the ν_3 energy levels lie close in energy to ν_1 levels of the same overall (rotational-vibrational) symmetry. The important pairs of this type are 818 (ν_3), 826 (ν_1) and 707 (ν_3), 735 (ν_1). The ν_3 and ν_1 bands being of the A and B type respectively, the level interaction occurs according to C type selection rules.

3. Coriolis interactions

The B type ν_1 band interacts strongly with an A type ν_3 band. The relative positions of the K_a levels of the two bands are shown for $J=10$ in figure 3b and for the 818 (ν), 826 (ν_1) and 707 (ν_3), 735 (ν_1) pairs of levels in figure 4. In ν_1 , $K_a=6$ and 7 lie below the interacting levels in the ν_3 band while for $K_a=8$, it lies above it. The resonance causes the levels of ν_1 to be first pushed down most strongly at $K_a=7$ while the corresponding levels of $K_a=6$ in ν_3 are pushed in the opposite direction. This

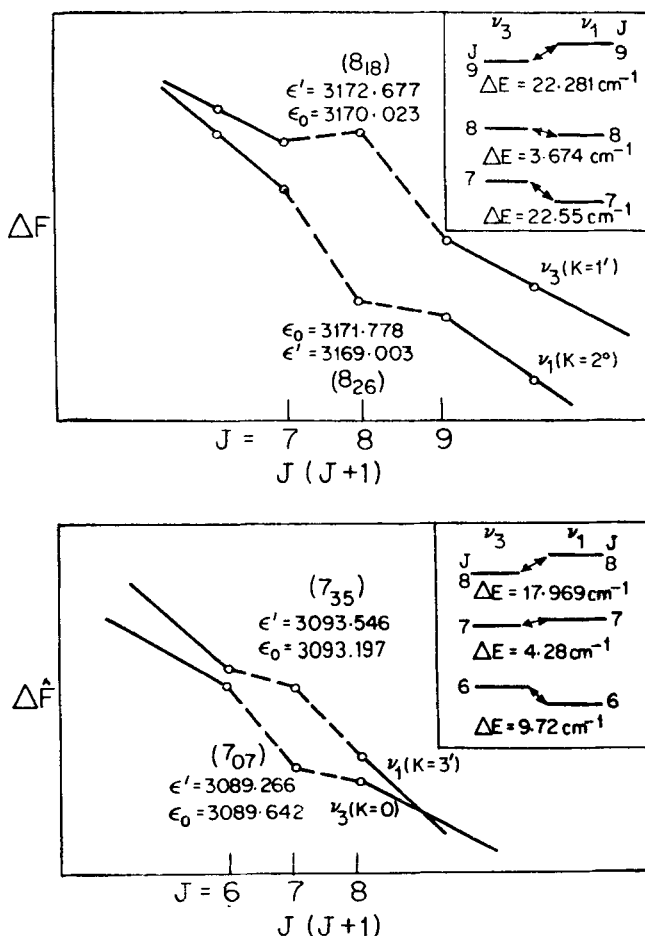


Figure 3a. Plot of ΔE versus $J(J+1)$ for interacting sub-bands of ν_1 and ν_3 bands
3b. Relative positions of Coriolis interacting levels of ν_1 and ν_3 bands for $J = 10$.

effect is clearly illustrated in figure 1 by the plots of $J(J+1)$ versus the energy difference, $\Delta E(J, K_a, K_c)$, between excited and ground state levels of the same quantum numbers. In the spectrum, this results in the Q_6 and Q_7 transitions being displaced towards lower frequency while Q_8 shades in opposite direction. This interaction also gives rise to energy borrowing (from ν_3 band) and forbidden transitions. The actual strength of the effect depends on the magnitude of the interaction constant connecting the states and the energy differences between their unperturbed positions. This kind of interaction occurs as the K_a levels come into resonance and then reverse their relative positions. When there are accidental degeneracies, a second type of effect occurs in which the crossing of J levels may occur within a given K_a sub-band (Brown and Hunt 1979). Figures 3a and 3b show the plot of relative positions of the interacting levels as well as graphs of the corresponding $\Delta E(J, K_a, K_c)$ versus $J(J+1)$. The level interaction in the first case takes place through $K_a=1$ and through $K_a=3$ in the other case. The $J=7$ and $J=8$ levels of ν_1 lies below the interacting level (826)

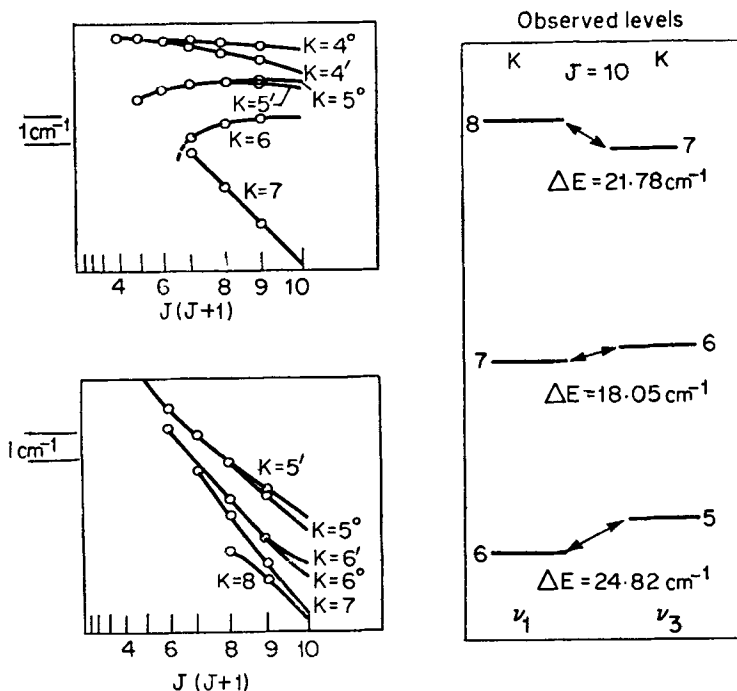


Figure 4. Level interaction and relative positions of levels for different J.

of ν_3 whereas $J=9$ lies above the corresponding level for ν_3 . In the spectrum, the two Q branches of these bands overlap as a result of this interaction. The transitions of P_{Q_8} and P_{Q_9} are shifted to lower frequencies for ν_1 (reversal) whereas in ν_3 band spacing of the Q branch transition suddenly changes from 10.4 cm^{-1} to 9.4 cm^{-1} at $J=8$ and to 11.9 cm^{-1} at $J=9$. Similar changes take place in the neighbourhood of other pair of interacting levels. Another case of sub-band perturbation occurs for $K_a=6$ of ν_3 with $K_a=7$ of ν_1 . The 761 (762) level of ν_3 occurs at $3444.3863 \text{ cm}^{-1}$ and 770 (771) of ν_1 at 3434.9243 . The resonance is almost perfect as shown below and the assignments may as well be reversed.

| ν_3 | $E (\text{cm}^{-1})$ | ν_1 | $E (\text{cm}^{-1})$ |
|---------|----------------------|-----------|----------------------|
| 660 | — | 3351.6497 | |
| 761 | — | 3444.3836 | 770 3434.9243 |
| 862 | — | 3544.0161 | 871 3531.2272 |
| 963 | — | 3655.6804 | 972 3640.1089 |
| 1064 | — | 3779.4866 | 1073 3761.4356 |
| 1165 | — | 3915.6370 | 1174 3897.9838 |
| 1266 | — | 4064.3482 | 1275 4044.0052 |

This sub-band interaction results in energy borrowing from the ν_3 levels and as a result of it the R_{Q_7} transitions of ν_1 appear stronger. In addition Q_8 transitions of

ν_3 and R_Q , of ν_1 are all crowded together in the same region. The first Q branch transition from the 660 (ν_3) level which does not interact with any level of ν_1 occurs at $2769\cdot2418\text{ cm}^{-1}$ which is far removed from the next one at $2775\cdot5334$. Rest of the transitions upto $J=13$ are contained within $2777\cdot9282\text{ cm}^{-1}$.

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