

Difference Frequency Laser Spectroscopy of OH and OD: Simultaneous Fit of the Infrared and Microwave Lines

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The fundamental vibration rotation bands of OH and OD have been observed with an estimated accuracy of 0.001 cm^{-1} . Simultaneous fits of the infrared and microwave data are performed to improve the molecular constants in the $v = 0$ and $v = 1$ states. The correlated parameters γ_v and A_D are determined by combining the data for OH and OD. Some discussion is presented on the correlated molecular parameters.

INTRODUCTION

The OH radical is one of the most extensively studied free radicals in various frequency regions. In particular, the Λ -type doubling transition frequencies have been measured precisely by microwave and radio frequency techniques, molecular beam electric resonance, and electron paramagnetic resonance for both OH and OD. The earlier references can be found in Refs. (1-5). Infrared spectroscopy is not an exception either, although the activity in this region seems less extensive. The $v = 1 - 0$ band of OH has been observed among other sequence bands by Maillard *et al.* (6) by high-resolution Fourier transform spectroscopy. In spite of the claimed accuracy of their measurements, the results of the least-squares fit do not seem to be completely satisfactory. In the course of checking our Zeeman modulation difference frequency system with OH as a test molecule, discrepancies between their measurements and ours as large as 0.03 cm^{-1} were detected. This led us to the remeasurement of the $v = 1 - 0$ band of OH.

Amiot, *et al.* (7) observed $\Delta v = 2$ and 3 sequence bands of OD in emission by Fourier transform spectroscopy, and obtained the molecular constants and the term values for $v = 0$ to 5 states. However, the $v = 1 - 0$ band of OD has not been measured. The data for this isotopic species are important for determination of A_D and γ_v . Therefore, we have also measured the $v = 1 - 0$ band of OD to make our analysis complete.

Since the Λ -type doubling transition frequencies depend indirectly on the fine structure and the rotational energies, an accurate determination of such parameters as A_v , B_v , and D_v is essential for a reliable determination of the Λ -type doubling constants. For this reason, Coxon performed a merged least-squares fit and obtained a set of "optimum" molecular constants for OH (8). Recently, Brown and his co-workers determined improved molecular constants by combining the far-infrared LMR data with the existing EPR data (3, 4). In particular, they observed several

transitions between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states so that they could determine the spin-orbit coupling constant A_0 without assuming the optical data.

In the present paper, more accurate infrared transition frequencies observed here are subjected to a simultaneous least-squares fit with the existing microwave lines to improve the molecular constants, particularly in the $v = 1$ state, and the band origin. A few satellite lines ($^2\Pi_{1/2} \leftarrow ^2\Pi_{3/2}$) have also been observed to yield an independent determination of the spin-orbit coupling constants A_0 and A_1 . Some discussion will be made on the correlated molecular parameters.

EXPERIMENTAL DETAILS

The difference frequency laser spectrometer used in this work is essentially the same as in our previous work (9). The OH(OD) was generated in a dc discharge through $\text{H}_2\text{O}(\text{D}_2\text{O})$ at a pressure of about 600 mTorr, and the discharge current was 30–60 mA. Figures 1 and 2 show examples of the observed signals. The signals were simultaneously recorded with Zeeman modulation (upper trace) and the frequency modulation (lower trace). The transition wavenumbers were calibrated with H_2O (10), D_2O (11), or N_2O (12) lines. The accuracy of the wavenumber measurement was estimated to be 0.001 cm^{-1} . Figure 3 is an example of the transitions between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. The intensity of these lines is approximately 1% of the corresponding main lines and is about 0.2% absorption with a 16-m effective path length. The minimum detectable absorption coefficient is estimated to be about $1 \times 10^{-7} \text{ cm}^{-1}$.

ANALYSIS

The effective rotational Hamiltonian used in this analysis is given in the Appendix. Several comments on the definitions of the parameters can also be found in the Appendix. In the calculation of the hyperfine splittings $\Delta J = \pm 1$ interactions were included, but $\Delta J = \pm 2$ interactions of the electric quadrupole interactions were neglected. The higher order hyperfine interaction terms, d_D , C_I , and C'_I were retained.

The simultaneous least-squares fits were made with all of the available Λ -doubling

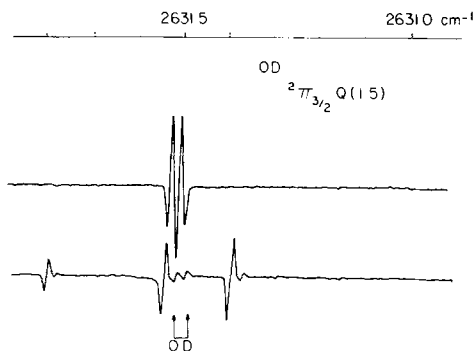


FIG. 1. The $Q(15)$ transitions in $^2\Pi_{3/2}$ state of OD recorded with Zeeman modulation technique. The lower trace recorded with frequency modulation shows D_2O lines in addition to OD lines.

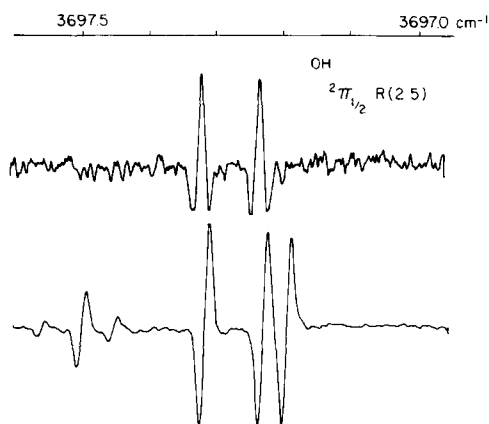


FIG. 2. The $R(2,5)$ transitions in $^2\Pi_{1/2}$ state of OH. Zeeman modulation is less efficient for the lines in $^2\Pi_{1/2}$ state. The additional lines in the lower trace are H_2O lines.

transition frequencies in the $v = 0$ and $v = 1$ states and the infrared data obtained in the present work. One of the higher order Λ -doubling parameters q_L which Coxon included as a variable parameter was found insignificant. In the $v = 1$ state, p_H was held fixed at its ground state value. In OD, p_L was also found insignificant. Only p , q , p_D , and q_D were included as variable Λ -doubling parameters in the $v = 1$ state of OD because almost no direct measurements of the Λ -doubling frequencies were available except one derived from an EPR measurement (13). The centrifugal distortion constant H was held fixed at the value obtained by Coxon (8).

The weight factor (w_i) was taken in accord with estimated accuracy (σ_i); that is, $w_i = \sigma_i^{-2}$. The accuracy of the infrared measurement was assumed uniformly to be ± 30 MHz for both OH and OD, although the accuracy might vary slightly from line to line. Tables I and II list the observed wavenumbers of the $v = 1 \leftarrow 0$ transitions

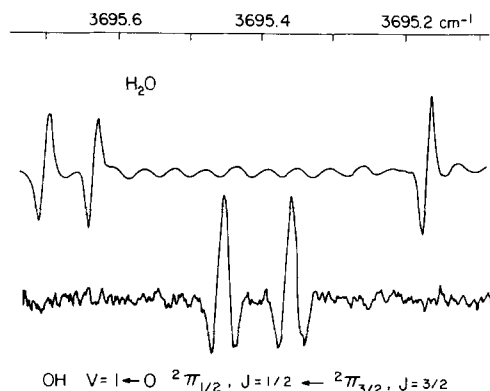


FIG. 3. The $P(1,5)$ transitions of the $^2\Pi_{1/2}$ - $^2\Pi_{3/2}$ satellite band of OH recorded with Zeeman modulation with the detection time constant of 0.4 sec. The upper trace was recorded simultaneously with frequency modulation. The wiggles of the trace are the interference fringes, and the OH lines are not noticeable.

TABLE I
Observed Wavenumbers of the $v = 1 \leftarrow 0$ Band of OH ($X^2\Pi$) in cm^{-1}

| Transition | ν_0 | $(O-C) \times 10^4$ | ν_0 | $(O-C) \times 10^4$ |
|------------|-------------------------------|---------------------|-------------------------------|---------------------|
| | $[^2\Pi_{3/2} - ^2\Pi_{3/2}]$ | | $[^2\Pi_{1/2} - ^2\Pi_{1/2}]$ | |
| P(7.5) f | 3280.0358 | -6 | | |
| e | 3280.7435 | 1 | | |
| P(6.5) f | 3323.9774 | -1 | 3287.8775 | 4 |
| e | 3324.5778 | 4 | 3287.4786 | 1 |
| P(5.5) f | 3366.5479 | -5 | 3333.3853 | 2 |
| e | 3367.0385 | 1 | 3333.0893 | 2 |
| P(4.5) f | 3407.6105 | -15 | 3378.0779 | 0 |
| e | 3407.9890 | 2 | 3377.8873 | -5 |
| P(3.5) f | 3447.0135 | 16 | 3422.0142 | -2 |
| e | | | 3421.9320 | -2 |
| P(2.5) f | 3484.5991 | 5 | | |
| e | 3484.7500 | 14 | | |
| P(1.5) f | | | 3507.7519 | -9 |
| e | | | 3507.8613 | -9 |
| Q(2.5) ef | 3565.2806 | 10 | | |
| Q(1.5) ef | 3568.4153 | -2 | | |
| fe | 3568.5211 | -13 | | |
| Q(0.5) ef | | | 3568.9066 | 25 |
| fe | | | 3569.2114 | -13 |
| R(2.5) e | | | 3697.3134 | 12 |
| f | | | 3697.2270 | 17 |
| R(3.5) e | 3708.7027 | -10 | 3728.6253 | 0 |
| f | 3708.9980 | -14 | 3728.4519 | -5 |
| R(4.5) e | | | 3757.7900 | -5 |
| f | | | 3757.5408 | -12 |
| R(5.5) e | 3763.9123 | 1 | | |
| f | 3764.3359 | 12 | | |
| | $[^2\Pi_{1/2} - ^2\Pi_{3/2}]$ | | | |
| P(1.5) e | 3695.3555 | -20 | | |
| f | 3695.4522 | -5 | | |
| Q(2.5) ef | 3767.2883 | 7 | | |
| fe | 3767.7560 | 14 | | |

for OH and for OD, respectively. The rms deviations of the fit are 29 MHz for OH and 18 MHz for OD. Table III reproduces the Λ -doubling transition frequencies of OH in both the $v = 0$ and $v = 1$ states. The quality of the fit is essentially the same

TABLE II

Observed Wavenumbers of the $v = 1 \leftarrow 0$ Band of OD ($X^2\Pi$) in cm^{-1}

| Transition | ν_0 | $(0-C) \times 10^4$ | ν_0 | $(0-C) \times 10^4$ |
|------------|-------------------------------|---------------------|-------------------------------|---------------------|
| | $[^2\Pi_{3/2} - ^2\Pi_{3/2}]$ | | $[^2\Pi_{1/2} - ^2\Pi_{1/2}]$ | |
| P(5.5) f | 2523.4996 | -6 | 2510.7439 ^a | -8 |
| e | 2523.6220 | 0 | | 15 |
| P(4.5) f | 2544.6304 | 0 | 2533.7584 | -4 |
| e | 2544.7185 | 2 | 2533.7876 | 6 |
| P(3.5) f | 2565.1626 | 5 | 2556.3879 | 2 |
| e | 2565.2197 | 9 | 2556.4436 | -5 |
| P(2.5) f | 2585.0930 | 0 | 2578.6071 | -1 |
| e | 2585.1231 | 1 | 2578.6867 | -5 |
| P(1.5) f | | | 2600.3770 | -1 |
| e | | | 2600.4733 | -2 |
| Q(3.5) fe | 2628.6423 | 0 | | |
| Q(2.5) ef | 2630.2434 | -4 | | |
| fe | 2630.3202 | -8 | | |
| Q(1.5) ef | 2631.4986 | 2 | | |
| fe | 2631.5185 | 0 | | |
| Q(0.5) ef | | | 2631.7782 | -11 |
| fe | | | 2631.9833 | 0 |
| R(0.5) e | | | 2662.3726 | 14 |
| f | | | 2662.4594 | 8 |
| R(1.5) e | | | 2681.7093 | 0 |
| f | 2676.6966 | 2 | 2681.7765 | 5 |
| R(2.5) e | 2693.6177 | -4 | 2700.3025 | 1 |
| f | 2693.6671 | -3 | 2700.3435 | 0 |
| R(3.5) e | 2710.1437 | 7 | 2718.1297 | -6 |
| f | 2710.2165 | 1 | 2718.1440 | 2 |
| R(4.5) e | 2726.2240 | -2 | 2735.1875 | -12 |
| f | 2726.3204 | -13 | 2735.1735 | -10 |
| R(5.5) e | 2741.8339 | 7 | 2751.5007 | 9 |
| f | 2741.9536 | 4 | 2751.4607 | 12 |
| R(6.5) e | 2756.9381 | 4 | 2767.0219 | -2 |
| f | 2757.0782 | 2 | 2766.9571 | -3 |
| R(7.5) e | 2771.5055 | -5 | | |
| | $[^2\Pi_{1/2} - ^2\Pi_{3/2}]$ | | | |
| P(1.5) e | 2762.8754 | 5 | | |
| f | 2762.9645 | -5 | | |

^a unresolved

TABLE III

A-Type Doubling Transition Frequencies of OH ($X^2\Pi$) in $v = 0$ and $v = 1$ States (in MHz)

| J | F'+F | ν_0 | $\nu_0 - \nu_c$ | Ref. |
|-------------------|-------|----------------|-----------------|------|
| $2\Pi_{3/2}, v=0$ | | | | |
| 1.5 | 1f+2e | 1612.23101(20) | 0.00011 | a |
| | 1f+1e | 1665.40184(20) | -0.00004 | a |
| | 2f+2e | 1667.35903(20) | 0.00014 | a |
| | 2f+1e | 1720.52998(20) | 0.00011 | a |
| 2.5 | 2f+3e | 6016.746(5) | -0.0047 | b |
| | 2f+2e | 6030.7485(2) | -0.0001 | c |
| | 3f+3e | 6035.0932(2) | -0.0001 | c |
| | 3f+2e | 6049.084(8) | -0.0073 | b |
| 3.5 | 3e+4e | 7.435(15) | -0.0402 | d |
| | 4f+3e | 13433.930(25) | -0.0121 | e |
| | 3f+3e | 13434.6374(2) | 0.0001 | c |
| | 4f+4e | 13441.4173(2) | 0.0001 | c |
| 4.5 | 4f+5f | 12.315(15) | -0.0008 | d |
| | 4e+5e | 21.320(15) | -0.0016 | d |
| | 5f+4e | 23805.297(10) | -0.0025 | d |
| | 4f+4e | 23817.6153(2) | 0.0000 | f |
| | 5f+5e | 23826.6211(2) | 0.0000 | f |
| | 4f+5e | 23838.933(10) | -0.0039 | d |
| 5.5 | 6f+5e | 36963.48(3) | -0.0069 | e |
| | 5f+5e | 36983.47(2) | -0.0057 | e |
| | 6f+6e | 36994.43(2) | 0.0248 | e |
| | 5f+6e | 37014.42(3) | 0.0260 | e |
| 6.5 | 7f+6e | 52696.72(3) | 0.0315 | e |
| | 6f+6e | 52722.04(2) | 0.0261 | e |
| | 7f+7e | 52734.56(2) | 0.0001 | e |

^aJ.J. Ter Meulen and A. Dymanus, *Astrophys. J.* **172**, L21 (1972).^bH.E. Radford, *Rev. Sci. Instrum.* **39**, 1687 (1968).^cJ.J. Ter Meulen, W.L. Meerts, G.W.M. van Mierlo, and A. Dymanus, *Phys. Rev. Lett.* **36**, 1031 (1976).^dJ.L. Destombes and C. Marliere, *Chem. Phys. Lett.* **34**, 532 (1975).^eJ.L. Destombes, G. Journel, C. Marliere, and F. Rohart, *C.R. Acad. Sci., Ser. B*, **280**, 809 (1975).^fJ.J. Ter Meulen, Ph.D. Thesis. Katholieke Universiteit, Nijmegen, The Netherlands (1976).^gJ.A. Ball, D.F. Dickinson, C.A. Gottlieb, and H.E. Radford, *Astron. J.* **75**, 762 (1970).^hW.L. Meerts and A. Dymanus, *Can. J. Phys.* **53**, 2123 (1975).ⁱW.L. Meerts and A. Dymanus, *Chem. Phys. Lett.* **23**, 45 (1973).^jJ.L. Destombes, B. Lemoine, and C. Marliere-Demuynck, *Chem. Phys. Lett.* **60**, 493 (1979).

TABLE III—Continued

| J | F'+F | ν_0 | $\nu_0 - \nu_c$ | Ref. |
|--------------------|---------|---------------|-----------------|----------|
| $^2\Pi_{1/2}, v=0$ | | | | |
| 7.5 | 6f+7e | 52759.89(3) | 0.0047 | e |
| | 7f+7e | 70845.08(2) | 0.0129 | e |
| | 8f+8e | 70858.93(2) | -0.0224 | e |
| $^2\Pi_{1/2}, v=0$ | | | | |
| 0.5 | 0f+1e | 4660.242(3) | 0.0006 | b |
| | 1f+1e | 4750.656(3) | -0.0012 | b |
| | 1f+0e | 4765.562(3) | -0.0016 | b |
| 1.5 | 1f+2e | 7749.909(5) | -0.0042 | g |
| | 1f+1e | 7761.747(5) | 0.0007 | g |
| | 2f+2e | 7820.125(5) | 0.0019 | g |
| | 2f+1e | 7831.962(5) | 0.0058 | g |
| 2.5 | 2f+3e | 8118.051(5) | -0.0073 | h |
| | 2f+23 | 8135.870(5) | 0.0015 | h |
| | 3f+3e | 8189.587(5) | 0.0011 | h |
| | 3f+2e | 8207.402(5) | 0.0058 | h |
| 3.5 | 3f+4e | 5449.436(5) | -0.0082 | h |
| | 3f+3e | 5473.045(5) | 0.0054 | h |
| | 4f+4e | 5523.438(5) | -0.0052 | h |
| | 4f+3e | 5547.042(5) | 0.0034 | h |
| 4.5 | 4e+5f | 88.9504(10) | 0.0005 | i |
| | 5e+5f | 117.1495(10) | -0.0004 | i |
| | 4e+4f | 164.7960(10) | 0.0000 | i |
| | 5e+4f | 192.9957(10) | -0.0003 | i |
| 5.5 | 6e+6f | 8534.86(2) | 0.0197 | e |
| | 5e+5f | 8580.17(2) | 0.0336 | e |
| 6.5 | 7e+7f | 19518.612(20) | -0.0089 | e |
| | 6e+6f | 19561.897(20) | -0.0020 | e |
| 7.5 | 8e+8f | 32879.80(5) | 0.0154 | <u>1</u> |
| | 7e+7f | 32921.35(5) | 0.0062 | <u>1</u> |
| 8.5 | 9e+9f | 48454.04(5) | 0.0101 | <u>1</u> |
| | 8e+8f | 48493.98(5) | -0.0452 | <u>1</u> |
| 9.5 | 10e+10f | 66094.76(5) | 0.0269 | <u>1</u> |
| | 9e+9f | 66133.35(5) | -0.0144 | <u>1</u> |
| $^2\Pi_{3/2}, v=1$ | | | | |
| 1.5 | 1f+2e | 1489.438(3) | -0.0008 | <u>5</u> |
| | 1f+1e | 1536.944(3) | -0.0041 | <u>5</u> |
| | 2f+2e | 1538.702(3) | -0.0025 | <u>5</u> |
| | 2f+1e | 1586.213(3) | -0.0008 | <u>5</u> |
| 2.5 | 2f+3e | 5583.476(7) | 0.0018 | <u>5</u> |
| | 2f+2e | 5594.246(5) | 0.0045 | <u>5</u> |
| | 3f+3e | 5598.168(5) | 0.0015 | <u>5</u> |
| | 3f+2e | 5608.935(6) | 0.0012 | <u>5</u> |

TABLE III—Continued

| J | F ¹ +F | ν_0 | $\nu_0 - \nu_c$ | Ref. |
|-------------------|-------------------|---------------|-----------------|--------------|
| 3.5 | 4f+3e | 12520.8(3) | 0.2815 | <u>1</u> |
| | 3f+3e | 12524.1(3) | 0.1148 | <u>1</u> |
| | 4f+4e | 12530.1(3) | -0.0485 | <u>1</u> |
| | 3f+4e | 12533.8(3) | 0.1847 | <u>1</u> |
| 4.5 | 4f+4e | 22296.57(14) | -0.0807 | <u>1</u> , j |
| | 5f+5e | 22304.86(14) | -0.0195 | <u>1</u> , j |
| 5.5 | 5f+5e | 34738.215(50) | -0.0256 | <u>1</u> , j |
| | 6f+6e | 34748.275(50) | 0.0087 | <u>1</u> , j |
| 6.5 | 6f+6e | 49650.59(5) | 0.0134 | <u>1</u> , j |
| | 7f+7e | 49662.09(5) | -0.0273 | <u>1</u> , j |
| 7.5 | 7f+7e | 66851.04(10) | -0.0057 | j |
| | 8f+8e | 66863.88(10) | 0.0383 | j |
| $2\Pi_{1/2}, v=1$ | | | | |
| 0.5 | 0f+1e | 4449.064(5) | 0.0004 | <u>5</u> |
| | 1f+1e | 4537.381(5) | 0.0001 | <u>5</u> |
| | 1f+0e | 4553.998(5) | 0.0004 | <u>5</u> |
| 1.5 | 1f+2e | 7454.592(6) | -0.0026 | <u>5</u> |
| | 1f+1e | 7467.323(8) | 0.0033 | <u>5</u> |
| | 2f+2e | 7522.842(6) | 0.0023 | <u>5</u> |
| | 2f+1e | 7535.563(5) | -0.0018 | <u>5</u> |
| 2.5 | 2f+2e | 7937.2(5) | 0.6400 | <u>1</u> |
| | 3f+3e | 7988.5(5) | 0.7680 | <u>1</u> |

as that of the fit by Coxon *et al.* (1). Table IV is the corresponding table for OD. One Λ -doubling transition frequency in the excited vibrational state of OD measured by Rashid *et al.* with EPR technique (13) was also included in the fit.

From the least-squares fit, an almost linear relation between the correlated parameters A_D and γ_v was determined as shown in Fig. 4. A similar relation was obtained for OD. The curve for OD may be shifted to give the curve shown in Fig. 4 by using the isotope relation. The crossing point gives the most reasonable values of A_D and γ_v for OH, and the values are transformed back to those for OD with the isotope relation. In Fig. 4, the dashed lines show the error limit that corresponds to one standard error obtained from the least squares fit with either A_D or γ_v held fixed. The shaded area indicates the estimated errors of A_D and γ_v . The point marked by B shows the values for these parameters determined by Brown and his co-workers (3) and the point marked by CF indicates the values calculated by Coxon and Foster (14).

The indeterminacy of the parameters A_D and γ_v also affects the determination of the "off-diagonal" molecular constants. The determinable combinations of the correlated parameters are

$$(\tilde{A}_v - 2\tilde{B}_v)A_D + (\tilde{B}_v - \frac{1}{2}\gamma_v)^2 = \text{const.} \quad (1)$$

$$\tilde{p}_v A_D - 2\tilde{q}_v(\tilde{B}_v - \frac{1}{2}\gamma_v) = \text{const.} \quad (2)$$

TABLE IV
 A-Type Doubling Transition Frequencies of OD ($X^2\Pi$) in $v = 0$ and $v = 1$ States (in MHz)

| J | F' + F | ν_0 | $\nu_0 - \nu_c$ | Ref. |
|-------------------|----------|---------------|-----------------|------|
| $2\Pi_{3/2}, v=0$ | | | | |
| 1.5 | 1.5+ 2.5 | 298.0970(10) | -0.0005 | a |
| | 0.5+ 1.5 | 303.0320(20) | 0.0000 | a |
| | 0.5+ 0.5 | 310.1445(5) | 0.0001 | a |
| | 1.5+ 1.5 | 310.2147(5) | -0.0004 | a |
| | 2.5+ 2.5 | 310.3627(10) | -0.0003 | a |
| | 1.5+ 0.5 | 317.3290(40) | 0.0016 | a |
| | 2.5+ 1.5 | 322.4800(20) | -0.0005 | a |
| 2.5 | 2.5+ 3.5 | 1185.8712(10) | 0.0004 | a |
| | 1.5+ 2.5 | 1186.9986(30) | -0.0012 | a |
| | 1.5+ 1.5 | 1190.5659(2) | 0.0000 | a |
| | 2.5+ 2.5 | 1190.7741(2) | 0.0001 | a |
| | 3.5+ 3.5 | 1191.1047(2) | 0.0000 | a |
| | 2.5+ 1.5 | 1194.3390(10) | -0.0011 | a |
| | 3.5+ 2.5 | 1196.0060(30) | -0.0019 | a |
| 3.5 | 2.5+ 3.5 | 2820.8514(20) | -0.0027 | a |
| | 3.5+ 4.5 | 2821.0857(20) | -0.0017 | a |
| | 2.5+ 2.5 | 2822.0007(20) | 0.0001 | a |
| | 3.5+ 3.5 | 2822.3883(20) | 0.0022 | a |
| | 3.5+ 2.5 | 2823.5328(20) | 0.0002 | a |
| | 4.5+ 3.5 | 2824.2276(20) | -0.0004 | a |
| 4.5 | 3.5+ 3.5 | 5304.015(5) | -0.0027 | b |
| | 5.5+ 4.5 | 5304.359(5) | 0.0030 | b |
| | 4.5+ 4.5 | 5304.600(5) | -0.0023 | b |
| | 3.5+ 4.5 | 5304.681(5) | 0.0041 | b |
| | 5.5+ 5.5 | 5305.372(5) | 0.0004 | b |
| | 4.5+ 5.5 | 5305.619(5) | 0.0011 | b |
| 5.5 | 4.5+ 4.5 | 8671.60(8) | 0.0231 | c |
| | 5.5+ 5.5 | 8672.37(8) | 0.0023 | c |
| | 6.5+ 6.5 | 8673.35(8) | -0.0129 | c |
| 6.5 | 5.5+ 5.5 | 12917.08(8) | -0.0232 | c |
| | 6.5+ 6.5 | 12918.13(8) | 0.0336 | c |
| | 7.5+ 7.5 | 12919.33(8) | 0.0219 | c |
| 7.5 | 6.5+ 6.5 | 18009.46(8) | -0.0246 | c |
| | 7.5+ 7.5 | 18010.63(8) | -0.0401 | c |
| | 8.5+ 8.5 | 18012.13(8) | 0.0465 | c |
| 8.5 | 7.5+ 7.5 | 23907.08(8) | -0.0211 | c |
| | 8.5+ 8.5 | 23908.44(8) | -0.0248 | c |
| | 9.5+ 9.5 | 23910.04(8) | -0.0223 | c |

^aW.L. Meerts and A. Dymanus, *Astrophys. J.* **180**, L93 (1973).

^bW.L. Meerts and A. Dymanus, *Can. J. Phys.* **53**, 2123 (1975).

^cR.A. Beaudet and R.L. Poynter, *J. Phys. Chem. Ref. Data*, **7**, 311-362 (1978).

TABLE IV—Continued

| J | F' + F | ν_0 | $\nu_0 - \nu_c$ | Ref. |
|--------------------|-----------|---------------|-----------------|------|
| 9.5 | 8.5+ 8.5 | 30565.42(8) | 0.0068 | c |
| | 9.5+ 9.5 | 30566.95(8) | 0.0104 | c |
| | 10.5+10.5 | 30568.72(8) | 0.0173 | c |
| 10.5 | 9.5+ 9.5 | 37940.73(8) | -0.0182 | c |
| | 10.5+10.5 | 37942.42(8) | -0.0013 | c |
| | 11.5+11.5 | 37944.35(8) | 0.0180 | c |
| $^2\Pi_{1/2}, v=0$ | | | | |
| 0.5 | 0.5+ 1.5 | 3090.2163(10) | -0.0004 | a |
| | 0.5+ 0.5 | 3093.6057(10) | 0.0003 | a |
| | 1.5+ 1.5 | 3111.1414(10) | 0.0003 | a |
| | 1.5+ 0.5 | 3114.5294(10) | -0.0004 | a |
| 1.5 | 0.5+ 1.5 | 5887.282(5) | -0.0005 | b |
| | 0.5+ 0.5 | 5887.741(5) | 0.0012 | b |
| | 1.5+ 2.5 | 5894.179(5) | -0.0011 | b |
| | 1.5+ 1.5 | 5894.680(5) | 0.0014 | b |
| | 1.5+ 0.5 | 5895.135(5) | -0.0009 | b |
| | 2.5+ 2.5 | 5906.215(5) | 0.0020 | b |
| | 2.5+ 1.5 | 5906.712(5) | 0.0005 | b |
| 2.5 | 1.5+ 2.5 | 8109.994(5) | 0.0004 | b |
| | 1.5+ 1.5 | 8110.717(5) | 0.0001 | b |
| | 2.5+ 3.5 | 8117.228(5) | -0.0011 | b |
| | 2.5+ 2.5 | 8118.013(5) | 0.0028 | b |
| | 2.5+ 1.5 | 8118.733(5) | -0.0005 | b |
| | 3.5+ 3.5 | 8128.181(5) | -0.0005 | b |
| 3.5 | 3.5+ 2.5 | 8128.961(5) | -0.0017 | b |
| | 2.5+ 2.5 | 9578.90(8) | -0.0324 | c |
| | 3.5+ 3.5 | 9586.32(8) | 0.0064 | c |
| 4.5 | 4.5+ 4.5 | 9595.74(8) | -0.0161 | c |
| | 3.5+ 3.5 | 10192.21(8) | -0.0135 | c |
| | 4.5+ 4.5 | 10199.56(8) | -0.0056 | c |
| 5.5 | 5.5+ 5.5 | 10208.50(8) | 0.0154 | c |
| | 4.5+ 4.5 | 9914.70(8) | -0.0042 | c |
| | 5.5+ 5.5 | 9921.95(8) | 0.0083 | c |
| 6.5 | 6.5+ 6.5 | 9930.44(8) | 0.0057 | c |
| $^2\Pi_{3/2}, v=1$ | | | | |
| 1.5 | ----- | 292.28(22) | 0.0327 | 13 |

$$2(a + b + c)A_D - 2b(\tilde{B}_v - \frac{1}{2}\gamma_v) = \text{const.} \quad (3)$$

$$dA_D + 2C'(\tilde{B}_v - \frac{1}{2}\gamma_v) = \text{const.} \quad (4)$$

All the "diagonal" parameters such as $\tilde{A}_v - 2\tilde{B}_v$, \tilde{p}_v , a , $b + c$, and d are well determined from the least-squares fit. The first equation is well known as pointed out by Veseth (15) and later discussed in detail by Brown and Watson (16). Similar relations are obtained for higher order terms, but even in OH only these correlations are important.

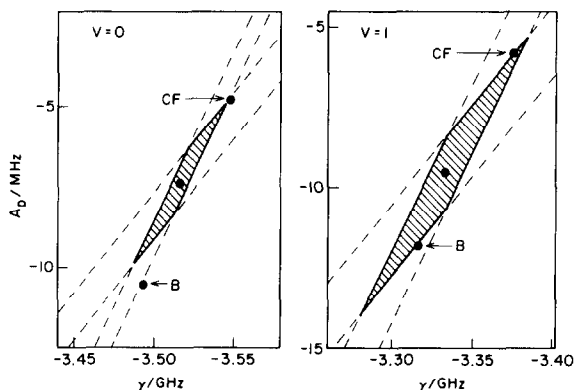


FIG. 4. The relationship between γ_v and A_D obtained from the least-squares fit. The dashed lines indicate $\pm 1\sigma$ limits. The shallower lines are obtained from the fit of OD by using isotope relations. The full circle in the middle of the shaded area indicates the values for γ_v and A_D listed in Tables V and VI. The points marked by B and CF are the values determined by Brown *et al.* (4) and Coxon and Foster (14), respectively.

Because of these correlations, the determination of \tilde{q}_v , b , and C'_l depends on the fixed value of A_D or γ_v . The systematic errors to be transferred from the uncertainties of A_D and γ_v can be much larger than the statistical errors obtained by fixing either A_D or γ_v . In principle, any parameter among the five parameters A_D , γ_v , \tilde{q}_v , b , and C'_l can be fixed to determine the remaining parameters. Therefore, one should be careful in choosing the set of adjustable parameters. One may ask if the higher order hyperfine doubling term C'_l is really significant. If C'_l is neglected, the same quality of fit can be obtained if both A_D and γ_v are allowed to vary. In this case obviously we have four parameters determinable from the four linear combinations given by Eqs. (1)–(4).

The molecular constants determined by the least-squares fit are summarized in Tables V and VI for OH and OD respectively. Errors (1σ) are indicated in parentheses to the last digits of the constants, except for A_D , γ_v , and \tilde{q}_v . The errors for A_D and γ_v are the upper and lower limits shown in Fig. 4, and the error in \tilde{q}_v due to these uncertainties of A_D and γ_v is given by

$$\delta\tilde{q}_v = (\tilde{p}_v\delta A_D + \tilde{q}_v\delta\gamma_v)/2(\tilde{B}_v - \frac{1}{2}\gamma_v). \quad (5)$$

The signs of the uncertainties should be taken consistently. Similar systematic uncertainties for b and C'_l are estimated by equations similar to Eq. (5) derived from Eqs. (3) and (4). However, these uncertainties are smaller than the statistical error, and are not listed in the tables. The band origin is also affected by the choice of A_D as

$$\delta\nu_0 = \delta A_D(v=1) - \delta A_D(v=0). \quad (6)$$

This amounts to only 0.85 MHz and was neglected.

DISCUSSION

As pointed out above, several transition wavenumbers of OH measured in the present work have shown unexpectedly large differences from the previous Fourier

TABLE V
Molecular Constants of OH in $v = 0$ and $v = 1$ States ($X^2\Pi$) (in MHz)

| | $v=0$ | $v=1$ |
|-------------------|--|-------------------------------------|
| ν_0 | 107 015 052.(12) [3569.63788(39) cm^{-1}] | |
| \tilde{A} | -4 172 307.(17) | -4 180 179.(21) |
| \tilde{B} | 555 539.2(18) | 534 228.6(21) |
| D | 57.065(26) | 55.850(39) |
| D' | 57.530(36) | 56.488(69) |
| \tilde{p} | 4 732.0041(11) | 4 519.6952(40) |
| \tilde{p}_D | -0.112219(61) | -0.00978(61) |
| $p_H \times 10^4$ | -3.568(43) | [-3.56] |
| $p_L \times 10^7$ | 3.6(4) | [0.] |
| \tilde{q} | -1 160.013 \pm 0.025 ^a | -1 107.467 \pm 0.039 ^a |
| \tilde{q}_D | 0.221247(11) | 0.21688(22) |
| $q_H \times 10^4$ | -0.8152(21) | -0.756(38) |
| A_D | -7.3 \pm 1.8 ^a | -9.7 \pm 2.7 ^a |
| γ | -3517. \pm 17 ^a | -3333. \pm 26 ^a |
| $a+(b+c)/2$ | 93.0820(26) | 85.2984(78) |
| $a-(b+c)/2$ | 79.1407(32) | 78.8471(64) |
| b | -116.7114(66) | -118.885(20) |
| d | 56.6485(31) | 53.795(10) |
| d_D | -0.02275(14) | -0.0260(34) |
| C_I | -0.09959(51) | -0.0980(19) |
| C_I' | 0.01828(8) | 0.0148(36) |

^aSee text for discussions on the uncertainties.

transform measurements. Most of them are the R -branch lines and are badly overlapped by lines of H_2O . Zeeman modulation technique is useful in such a case and enables us to pick out OH lines among stronger H_2O lines without affecting the frequency measurement. Several R -branch lines, however, could not be measured even with Zeeman modulation, because the overlapping H_2O transition absorbs infrared radiation almost completely so that no measurable power reaches the detector. The measurement of OD encountered a similar but less severe situation.

Since OH is classified as intermediate case (a) and (b) at fairly low- J states, a reasonably good determination of \tilde{A}_0 and \tilde{A}_1 is possible only with $^2\Pi_{1/2}$ - $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ - $^2\Pi_{3/2}$ subbands. The standard errors of \tilde{A}_0 and \tilde{A}_1 for OH thus determined were about 300 MHz. Nevertheless much better determination of those spin-orbit coupling constants was attained by observing a few transitions of the $^2\Pi_{1/2}$ - $^2\Pi_{3/2}$ band.

In Tables VII and VIII, comparisons of some major parameters with previous values are made. The differences in the definitions of the parameters were carefully examined and were corrected to be consistent. Our \tilde{A}_0 seems to correspond to Brown's

TABLE VI
Molecular Constants of OD in $v = 0$ and $v = 1$ States ($X^2\Pi$) (in MHz)

| | $v=0$ | $v=1$ |
|-------------------|--|-------------------------------|
| ν_0 | 78 905 177.1(55) [2632.06010(18) cm^{-1}] | |
| \tilde{A} | -4 169 530.(14) | -4 175 324.(14) |
| \tilde{B} | 296 125.16(113) | 287 865.77(85) |
| D | 16.113(26) | 15.886(15) |
| D' | 16.171(25) | 15.979(36) |
| \tilde{p} | 3 105.53255(35) | 3 009.5(34) |
| \tilde{p}_D | -0.118384(53) | -0.168(44) |
| $p_H \times 10^4$ | -0.191(47) | [0.] |
| \tilde{q} | -328.1081 \pm 0.014 ^a | -318.73(17) |
| \tilde{q}_D | 0.033010(27) | 0.0439(34) |
| $q_H \times 10^5$ | -0.631(27) | [0.] |
| A_D | -3.89 \pm 0.96 ^a | -5.20 \pm 1.45 ^a |
| γ | -1 875. \mp 15 ^a | -1 796. \mp 24 ^a |
| $a+(b+c)/2$ | 14.44115(75) | |
| $a-(b+c)/2$ | 12.16858(52) | |
| b | -17.8967(39) | |
| d | 8.76933(44) | |
| d_D | -0.00202(17) | |
| c_I | -0.00800(22) | |
| c_I' | 0.001093(88) | |
| eqQ | 0.2851(11) | |
| eqQ ₂ | -0.12336(97) | |

^aSee text for discussions on the uncertainties.

$A_v + \gamma_v$. The present value for the spin-orbit coupling constant \tilde{A}_0 for OH has turned out to be in between the values by Brown and his co-workers (3) and by Coxon (8), and is closer to Coxon's value. The origin of the unexpected difference in the rotational constant \tilde{B}_0 for OH from the previous values does not seem obvious. The agreement between the present and the previous values of \tilde{A}_0 and \tilde{B}_0 for OD is much better.

This paper probably provides the first direct reliable determination of $\alpha_A (= A_0 - A_1)$. It is considerably different from the previous values, both for OH and OD. Brown discussed that the ratio of α_A for OH and OD did not agree with the calculated reduced mass dependence. Now it is much closer to the expected ratio. As expected, the Λ -doubling constants mostly agree very well with the previous values. However, a few comments may be necessary. The Λ -doubling constant \tilde{p} defined in this work

TABLE VII

Comparison of Some Major Molecular Constants of OH (in MHz, Except for ν_0)

| | present | previous | Ref. |
|--|-----------------------------|----------------------------|------|
| ν_0 | 3569.63788 cm ⁻¹ | 3569.6432 cm ⁻¹ | (8) |
| | | 3569.6398 cm ⁻¹ | (6) |
| \tilde{A}_0 | -4172307. | -4172214. | (3) |
| | | -4172331. | (8) |
| $\alpha_A (= \tilde{A}_0 - \tilde{A}_1)$ | 7870.(18) | 7652(29) | (4) |
| | | 7955(63) | (8) |
| \tilde{B}_0 | 555539.2 | 555546.6 | (3) |
| | | 555546.9 | (8) |
| $\alpha_B (= \tilde{B}_0 - \tilde{B}_1)$ | 21310.7(13) | 21312.8 | (8) |
| γ_0 | -3517. | -3493.5 | (4) |
| A_D | -7.3 | -10.7 | (4) |
| P_0 | 4732.4893 | 4732.0585 | (1) |
| | | 4733.11516 | (2) |
| | | 4732.4491 | (8) |
| P_1 | 4520.1871 | 4519.7441 | (1) |
| | | 4520.1473 | (8) |
| P_{D0} | -0.333466 | -0.33343 | (1) |
| | | -0.333449 | (2) |
| | | -0.33348 | (8) |
| P_{D1} | -0.33666 | -0.3385 | (1) |
| | | -0.33993 | (8) |
| q_0 | -1159.8467 | -1162.4161 | (1) |
| | | -1159.991650 | (2) |
| | | -1159.55593 | (8) |
| q_1 | -1107.299 | -1109.8926 | (1) |
| | | -1106.9956 | (8) |
| q_{D0} | 0.221247 | 0.221166 | (1) |
| | | 0.2210160 | (2) |
| | | 0.220948 | (8) |
| q_{D1} | 0.21688 | 0.21756 | (1) |
| | | 0.21697 | (8) |

is a well-determined quantity independent of A_D or γ_v . In the previous formulations, the term in q appeared explicitly in the diagonal matrix element. As a result, the constant p in the previous studies has also a correlation with A_D or γ_v .

Our definitions of p_D and q_D are given in Table A2. The definitions by Brown *et al.* (2) are different by a factor of 2. Our p_D corresponds to $\frac{1}{2}(p_D + 2q_D)$ in Refs. (2-4, 8). The term $\pm q_D x(x^2 - 1)$, where $x = J + 1/2$, in the diagonal matrix elements seems to be missing in the fits in Ref. (1). Therefore, our \tilde{p}_D corresponds to $\frac{1}{2}p_D$ in Ref. (1).

The values of q_v given in Refs. (2-4, 8) should be interpreted as the effective parameters for $A_D = 0$. From Eq. (2), the effective parameter is given with a good approximation as

$$\tilde{q}_{\text{eff}}(A_D = 0) = \tilde{q} - \frac{\tilde{p}}{2B} A_D - \frac{\tilde{q}}{2B} (\gamma - \gamma_{\text{eff}}(A_D = 0)). \quad (7)$$

TABLE VIII

Comparison of Some Major Molecular Constants of OD (in MHz, Except for ν_0)

| | present | previous | Ref. |
|--|-----------------------------|----------------------------|------|
| ν_0 | 2632.06010 cm^{-1} | 2632.1050 cm^{-1} | (7) |
| | | 2632.12 cm^{-1} | (17) |
| \tilde{A}_0 | -4169530. | -4169523.97 | (4) |
| $\alpha_A (= \tilde{A}_0 - \tilde{A}_1)$ | 5794.(11) | 5571.(21) | (4) |
| | | 6377. | (7) |
| \tilde{B}_0 | 296125.1 | 296126.345 | (4) |
| $\alpha_B (= \tilde{B}_0 - \tilde{B}_1)$ | 8259.42(60) | 8265.5 | (7) |
| γ_0 | -1875. | -1851.5 | (4) |
| A_D | -3.89 | -5.57 | (4) |
| p_0 | 3105.63512 | 3105.90116 | (4) |
| p_{DO} | -0.151394 | -0.15136 | (4) |
| q_0 | -328.0324 | -327.97256 | (4) |
| q_{DO} | 0.033010 | 0.033020 | (4) |

However, the difference does not seem to be fully accounted for by making the correction according to the equation above. Particularly, the source of the rather large difference between the present q_v and that obtained in Ref. (1) is not clear.

The higher order vibration-rotation constants are not negligible for calculation of \tilde{B}_e . They were determined for OH to fit to the rotational constants \tilde{B}_0 and \tilde{B}_1 obtained in the present work and the rotational constants for the $v = 2$ to 5 states obtained by Coxon (8). In the calculation of \tilde{B}_e of OD, the correction was made by taking γ_e (17) into account. The second-order electronic contribution to the rotational constant, q_0^* , was estimated by using g_r obtained from EPR by Brown *et al.* (2). We obtained $q_0^* = -644 \pm 11$ MHz for OH and $q_0^* = -190 \pm 6$ MHz for OD. Although the experimental q^* 's are not the equilibrium values, we used these values for calculation of B_e without making further corrections. The equilibrium rotational constants and the equilibrium internuclear distances thus obtained are listed in Table IX.

The hyperfine interaction term C'_1 arises from the second-order cross term between $H'_{\text{hfs}} = a\mathbf{I} \cdot \mathbf{L}$ and $H'_r = -2\tilde{B}\mathbf{J} \cdot \mathbf{L}$ and is given by

$$H_{\text{eff}}(C'_1) = C'_1(J_+I_+e^{-2i\phi} + J_-I_-e^{2i\phi}) \quad (8)$$

where

$$C'_1 = -2 \sum_{n'=\Sigma} (-1)^s \langle n\Lambda = 1 | aL_+ | n'\Lambda = 0 \rangle \langle n'\Lambda = 0 | \tilde{B}L_- | n\Lambda = 1 \rangle / \Delta E_{nn'}. \quad (9)$$

TABLE IX

Equilibrium Rotational Constant and Equilibrium Internuclear Distance

| | \tilde{B}_e /MHz | B_e /MHz | $r_e/\text{\AA}$ |
|----|--------------------|-------------|------------------|
| OH | 566 320.1 | 566 964(11) | 0.969628(9) |
| OD | 300 268.0 | 300 458(6) | 0.969680(10) |

Therefore, C'_I may be estimated from the following relationship

$$C'_I \simeq -(\tilde{p} - 2\tilde{q})a/\tilde{A}, \quad (10)$$

and the estimated value turns out to be 0.15 MHz. This is about 10 times bigger than the value determined from the least-squares fit. The probable source of this difference is due to the use of a determined by the fit which is $Ng_I g \mu_0 \mu_N \langle \Pi \| I_{1Z} / r_{1I} r_{1I}^3 \| \Pi \rangle$ and not equal to $Ng_I g \mu_0 \mu_N \langle \Pi \| I_{1+} / r_{1I}^3 \| \Sigma \rangle$ (18). However, if a reliable estimate of this quantity C'_I can be obtained, one can determine A_D and γ_v separately by fixing C'_I at the estimated value.

APPENDIX

We assume a simplified form for spin-orbit and spin-rotation interactions as

$$H_{so} = A(r, R) \mathbf{L} \cdot \mathbf{S} \quad (A1)$$

$$H_{sr} = \gamma^{(1)}(r, R) \mathbf{N} \cdot \mathbf{S}, \quad (A2)$$

where r and R stand for the coordinates of electrons and nuclei, respectively. The effective Hamiltonian is obtained by using a similar method by Freed (18, 19). Among the terms in $S^2 - S_z^2$, only $\tilde{B}(S^2 - S_z^2)$ is retained in the rotational part, and other $S^2 - S_z^2$ terms and $B\langle L_x^2 + L_y^2 \rangle$ are included in the vibrational potential energy. The effective Hamiltonian in a $^2\Pi$ state up to the fourth order perturbation is expressed as

$$H_{\text{eff}}(R) = \tilde{A}(R) \Lambda S_z + \tilde{B}(R)(J^2 - J_z^2 + 1/2) - (\tilde{B}(R) - 1/2 \gamma(R))(J_+ S_- + J_- S_+) + 1/2[p(R)J_- S_- - q(R)J_z^2]e^{2i\phi} + 1/2[p(R)J_+ S_+ - q(R)J_z^2]e^{-2i\phi}, \quad (A3)$$

where the effective operators are defined as

$$\tilde{A}(R) = A + A' + A'' + \gamma^{(1)} \quad (A4)$$

$$\tilde{B}(R) = B + q^* \quad (A5)$$

$$\gamma(R) = \gamma^{(1)} - p^* \quad (A6)$$

$$p(R) = 2 \sum_{n'=\Sigma} (-1)^s \langle n\Lambda = 1 | (A + 2B)L_+ | n'\Lambda = 0 \rangle \times \langle n'\Lambda = 0 | BL_- | n\Lambda = 1 \rangle / \Delta E_{nn'} \quad (A7)$$

$$q(R) = 2 \sum_{n'=\Sigma} (-1)^s |\langle n\Lambda = 1 | BL_+ | n'\Lambda = 0 \rangle|^2 / \Delta E_{nn'} \quad (A8)$$

$$p^*(R) = \sum_{n'=\Sigma, \Delta} \langle n\Lambda | AL_\perp | n'\Lambda' \rangle \langle n'\Lambda' | BL_\perp | n\Lambda \rangle / \Delta E_{nn'} \quad (A9)$$

$$q^*(R) = \sum_{n'=\Sigma, \Delta} |\langle n\Lambda | BL_\perp | n'\Lambda' \rangle|^2 / \Delta E_{nn'}, \quad (A10)$$

where L_\perp is either $L_+ = L_x + iL_y$ or $L_- = L_x - iL_y$. The effective spin-orbit interaction constant \tilde{A} includes the second-order contributions (A' and A'') from $P_0 H_{so}(Q_0/a) H_{so} P_0$, $P_0 H_{so}(Q_0/a) H_r P_0$, and $P_0 H_r(Q_0/a) H_{so} P_0$ and the first-order spin-rotation interaction

term $\gamma^{(1)}$. After the vibrational perturbations (centrifugal distortion effects) are calculated, the Hamiltonian is obtained as shown in Table A1 in terms of the symmetrized Hund's case (a) bases. The definitions of the parameters are listed in Table A2.

Several comments may be necessary.

(1) D_v'' is not a determinable parameter. In the fits of OH and OD, D_v'' was constrained at $(2D_v' - D_v)$ by neglecting γ_D^2/D_v . An alternative method is to absorb D_v'' into \tilde{A}_v , \tilde{B}_v , and γ_v , and to redefine them.

(2) Instead of choosing D_v and D_v' as the variables, D_v and γ_D can be varied.

(3) In our present fit, q_D' was set equal to q_D .

(4) In deriving p_v , q_v , and p_D from the fitted parameters \tilde{p}_v , \tilde{q}_v , and \tilde{p}_D , p_D' is also assumed to be equal to p_D , and p_D'' is calculated with the relation given in Table A2.

(5) p_H , p_L , q_H , and q_L terms are added empirically.

(6) In our fits, we added the centrifugal terms in H by assuming the matrix elements given by Zare *et al.* (20).

(7) The centrifugal distortion parameters A_D , p_D , q_D , and γ_D are smaller by a factor of 2 than the corresponding ones by Brown and his co-workers.

(8) In Brown's formulation, $-\gamma_v$ appears as a diagonal matrix element in $^2\Pi_{1/2}$ state, but it does not in our formulation. Therefore, his $T_v - 1/2\gamma_v$ corresponds to our T_v , and his $A_v + \gamma_v$ to our \tilde{A}_v . This difference arises from the fact that he assumes $H_{sr} = \gamma\mathbf{N} \cdot \mathbf{S}$ but we assume $H_{sr} = \gamma^{(1)}\mathbf{N} \cdot \mathbf{S}$. We also eliminate $\gamma(S^2 - S_z^2)$ from the rotational part.

(9) Our \tilde{A}_v does not have any strong correlation with γ or A_D .

(10) Our effective \tilde{A}_v includes $\gamma^{(1)}$, the first-order spin-rotation interaction constant, but it is usually much smaller than γ .

Equations (1)–(4) in the text can be derived by the following straightforward method. The total Hamiltonian is written as

$$H_{\text{eff}} = H_{\text{rot}} \pm H_{\Lambda} + H_{\text{hf}} \pm H_{\text{hf}\Lambda}, \quad (\text{A11})$$

where

$$H_{\text{rot}} = \begin{bmatrix} a & c \\ c & b \end{bmatrix}, \quad H_{\Lambda} = \begin{bmatrix} a_{\Lambda} & c_{\Lambda} \\ c_{\Lambda} & b_{\Lambda} \end{bmatrix} \quad (\text{A12})$$

TABLE A1

Rotational Matrix^{a,b}

| | | |
|---------------|---|--|
| $^2\Pi_{3/2}$ | $T_v + \frac{1}{2}\tilde{A}_v - D_v'' + (\tilde{B}_v - D_v'' + A_D)(x^2 - 2)$ | $[\tilde{B}_v - \frac{1}{2}\gamma_v - 2D_v'(x^2 - 1)](x^2 - 1)^{\frac{1}{2}}$ |
| | $-D_v(x^2 - 2)^2$ | $\pm \frac{1}{2}[\tilde{q}_v + 2q_D(x^2 - 1) + q_H(x^2 - 1)^2 + q_L(x^2 - 1)^2]$ |
| | $\pm q_D'x(x^2 - 1)$ | $xx(x^2 - 1)^{\frac{1}{2}}$ |
| $^2\Pi_{1/2}$ | sym | $T_v - \frac{1}{2}\tilde{A}_v + D_v'' + (\tilde{B}_v - D_v'' - A_D)x^2 - D_vx^4$ |
| | | $\pm \frac{1}{2}(\tilde{p}_v + 2\tilde{p}_Dx^2 + p_Hx^4 + p_Lx^6)x$ |

^a $x = J + \frac{1}{2}$

^b $+$ sign applies to f-levels, and $-$ to e-levels.

TABLE A2
Definitions of the Parameters

| Parameter | Definition |
|---------------|--|
| \tilde{A}_v | $\langle v \tilde{A}(\xi) v \rangle$ |
| \tilde{B}_v | $\langle v \tilde{B}(\xi) v \rangle$ |
| \tilde{p}_v | $p_v + p_D^+ - 2q_D^+$, $p_v = \langle v p(\xi) v \rangle$ |
| \tilde{q}_v | $q_v + \frac{1}{2}p_D^+$, $q_v = \langle v q(\xi) v \rangle$ |
| D_v | $-\sum_{v'} \langle v \tilde{B}(\xi) v' \rangle ^2 / \Delta E_{vv'}$ |
| D_v^+ | $-\sum_{v'} \langle v \tilde{B}(\xi) v' \rangle \langle v' \tilde{B}(\xi) - \frac{1}{2}\gamma(\xi) v \rangle / \Delta E_{vv'}$, $= D_v + \frac{1}{2}\gamma_D$ |
| D_v^- | $-\sum_{v'} \langle v \tilde{B}(\xi) - \frac{1}{2}\gamma(\xi) v' \rangle ^2 / \Delta E_{vv'}$, $= D_v + \gamma_D + \gamma_D^2 / D_v$ |
| A_D | $\sum_{v'} \langle v \tilde{A}(\xi) v' \rangle \langle v' \tilde{B}(\xi) v \rangle / \Delta E_{vv'}$ |
| \tilde{p}_D | $p_D + q_D^+$, $p_D = \sum_{v'} \langle v p(\xi) v' \rangle \langle v' \tilde{B}(\xi) v \rangle / \Delta E_{vv'}$ |
| q_D | $\sum_{v'} \langle v q(\xi) v' \rangle \langle v' \tilde{B}(\xi) v \rangle / \Delta E_{vv'}$ |
| p_D^+ | $\sum_{v'} \langle v p(\xi) v' \rangle \langle v' \tilde{B}(\xi) - \frac{1}{2}\gamma(\xi) v \rangle / \Delta E_{vv'}$, $= p_D + p_D \gamma_D / 2D_v$ |
| p_D^- | $\sum_{v'} \langle v p(\xi) v' \rangle \langle v' \tilde{A}(\xi) v \rangle / \Delta E_{vv'}$, $= A_D p_D / D_v$ |
| q_D^+ | $\sum_{v'} \langle v q(\xi) v' \rangle \langle v' \tilde{B}(\xi) - \frac{1}{2}\gamma(\xi) v \rangle / \Delta E_{vv'}$, $= q_D + q_D \gamma_D / 2D_v$ |

and so on. Let

$$U = \begin{bmatrix} \cos \theta & \cos \theta \\ -\sin \theta & \sin \theta \end{bmatrix} \quad (A13)$$

be a transformation matrix that diagonalizes H_{rot} , where

$$\cos 2\theta = \frac{a - b}{\sqrt{(a - b)^2 + 4c^2}} \quad (A14)$$

and

$$\sin 2\theta = \frac{2c}{\sqrt{(a - b)^2 + 4c^2}}. \quad (A15)$$

Apply this transformation to the rest of the matrix. The trace of the matrix is a well-determinable quantity, if enough data are available both for $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. Therefore, we have to examine only the difference in the diagonal matrix elements. The difference in the diagonal elements of $UH_A\tilde{U}$ is given by

$$\begin{aligned} &\cos 2\theta \cdot (a_A - b_A) + 2 \sin 2\theta \cdot c_A \\ &= \{(a - b)(a_A - b_A) + 4cc_A\} \{(a - b)^2 + 4c^2\}^{-1/2}. \end{aligned} \quad (A16)$$

In general,

$$\begin{aligned} a - b &= \sum_{n=0}^{\infty} \alpha_n (x^2 - 1)^n, & c &= \sum_{n=0}^{\infty} \beta_n (x^2 - 1)^{n+1/2}, \\ a_A - b_A &= \sum_{n=0}^{\infty} \gamma_n x (x^2 - 1)^n, & c_A &= \sum_{n=0}^{\infty} \delta_n x (x^2 - 1)^{n+1/2}. \end{aligned} \quad (A17)$$

Therefore

$$(a-b)(a_{\Lambda}-b_{\Lambda})+4cc_{\Lambda} \\ = \sum_{m=0}^k \sum_{k=0}^{\infty} (\alpha_{m+1}\gamma_{k-m} + \alpha_m\gamma_{k-m+1} + 4\beta_m\delta_{k-m})x(x^2-1)^{k+1} + \alpha_0\gamma_0x. \quad (\text{A18})$$

It is found that

$$\sum_{m=0}^k (\alpha_{m+1}\gamma_{k-m} + \alpha_m\gamma_{k-m+1} + 4\beta_m\delta_{k-m}), \quad k = 0, 1, 2, \dots \quad (\text{A19})$$

are the combinations of the parameters that will be well determined. Equation (2) is one example where $k = 0$ of Eq. (A19). Equations (3) and (4) are obtained in the same way from H_{hf} and $H_{\text{hf}\Lambda}$, respectively. The well-known indeterminacy given by Eq. (1) is a special case of Eq. (A18):

$$(a-b)^2 + 4c^2 = \sum_{m=0}^k \sum_{k=0}^{\infty} (\alpha_{m+1}\alpha_{k-m} + \alpha_m\alpha_{k-m+1} + 4\beta_m\beta_{k-m})(x^2-1)^{k+1} + \alpha_0^2. \quad (\text{A20})$$

Equation (1) is the coefficient of the term in (x^2-1) .

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