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Diode Laser Spectroscopy of the ν_4 Band of NH_2OH and the ν_5 Band of NHDOD

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Doppler-limited spectroscopy of the ν_4 band (OH bend) of hydroxylamine NH_2OH has been carried out using a diode laser spectrometer in the range 1320 to 1400 cm^{-1}. Hydroxylamine is so close to being a symmetric rotor that in the $v_4 = 1$ excited state the rovibrational effects cause the b and c molecular axes to be interchanged relative to their orientation in the ground state. The recognition of this fact allowed earlier work on the ν_5 band (*1*) to be corrected. The ν_4 band is perturbed by Coriolis-type interactions with at least two other modes. These are (i) a mainly c-type interaction with the combination band ($\nu_6 + \nu_9$) and (ii) an a-type interaction with what is probably the very weak fundamental ν_8. Effective unperturbed parameters are calculated for the ν_4 band. Accurate constants have been obtained for the ν_5 band (NHD-wagging motion) of the partially deuterated form of hydroxylamine, NHDOD. These are the first gas-phase infrared data on any deuterated form of hydroxylamine. © 1988 Academic Press, Inc.

INTRODUCTION

A diode laser spectroscopy study of several bands of hydroxylamine (NH_2OH) has been recently reported from this laboratory (*1*). Spectroscopy was carried out on the ν_5 (1115 cm^{-1}) and ν_6 (895 cm^{-1}) fundamentals, the $2\nu_9$ overtone, the $3\nu_9 - \nu_9$ hot band, and the $\nu_5 - \nu_9$ difference band (all near 700 cm^{-1}) of hydroxylamine ($\nu_5 = NH_2$ wag, ν_6 = N–O stretch and ν_9 = OH torsion). Accurate molecular parameters were determined for the ground state, $v_6 = 1$, $v_9 = 1$, and $v_9 = 2$. The $v_5 = 1$ and $v_9 = 3$ states were mutually perturbed by a Coriolis-type interaction and in these cases effective rotational, distortion constants, and empirical perturbation parameters were determined.

In the present paper we report the extension of this work to the ν_4 band of NH_2OH near 1354 cm^{-1} (*2*) and also the first gas-phase infrared data for a deuterated form of hydroxylamine (NHDOD).

The ν_4 band of NH_2OH is perturbed by a Coriolis-type interaction between $v_4 = 1$ and two other vibrational states. One of these is almost certainly the ($v_6 = 1$, $v_9 = 1$) combination state. The second interaction is possibly between ν_4 and the fundamental ν_8. There is absolutely no direct spectroscopic information over ν_8.

The analysis of the ν_4 band also revealed that the a and the b axes of hydroxylamine are interchanged in the $v_4 = 1$ state relative to their orientation in the ground state. This effect is produced by the fact that the B and C rotational constants of hydroxylamine are very similar ($\kappa = -0.998$) so that the effects of rotational–vibrational interaction are sufficiently large to cause this interchange. Recognition of this possibility caused us to reappraise our analysis of the perturbed ν_5 band (*1*) and it is now clear

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that this effect was responsible for discrepancies which had remained with our original analysis of the ν_5 data.

As discussed previously (e.g., (*1*)) hydroxylamine takes up an energetically preferred configuration in which the hydrogen atom of the hydroxyl group is in a *trans* position relative to those of the amino group. As a result of this the barrier to the inversion of the amino group is high and no splittings from this source were observed either in the ground state microwave spectrum (*3*) or in the Doppler-limited infrared spectrum of the ν_5 (amino wag) band (*1*). Recent sub-Doppler measurements on several transitions of the ν_5 band (*4*) using a tunable CO_2 sideband laser system failed to resolve any splitting even though the resolution was estimated to be $\approx$100 kHz. This means that the hydroxylamine *trans* configuration is very stable indeed.

Hydroxylamine has been shown to function as an efficient optically pumped FIR laser (*5*). The deuterated species of hydroxylamine are in principle a potential source for many more FIR laser lines. All three hydrogens of the hydroxylamine molecule exchange readily with heavy water. Thus depending on the degree of enrichment of the D_2O used for exchange, the composition of the equilibrium mixture of six species (NH_2OH, NH_2OD, NHDOH, ND_2OH, NHDOD, and ND_2OD) may be varied. New FIR laser lines have been recently observed with hydroxylamine treated with heavy water (*6*). In this paper we report the first high-resolution infrared spectrum of any deuterated species of hydroxylamine. These data may be of relevance for the investigation of the mechanism of these new lasers.

EXPERIMENTAL PROCEDURE

The diode laser spectrometer used was based on the cold head assembly of Spectra Physics with diodes from the same firm. Measurements were carried out using a White cell with a 20-m path length and gas pressures in the range 0.1 to 0.5 Torr. A calibrated confocal étalon (FSR = 0.009811 cm^{-1}) and accurately measured absorption lines of NH_3 (*7*), H_2O (*8*), and SO_2 (*9*) were used to determine transition wavenumbers. Hydroxylamine was produced by warming hydroxylammonium phosphate to 80°C and was passed directly into the absorption cell.

A fully deuterated sample of hydroxylammonium phosphate was prepared by dissolving the normal substance in excess D_2O and then removing the water by evaporation. The procedure was then repeated. It was found that hydrogen atom exchange occurred rapidly with residual water within the White cell. The concentration of the desired deuterated species was maximized by treating the cell with H_2O/D_2O samples of varying composition.

OBSERVATIONS AND DISCUSSION

The ν_4 Band of NH_2OH

The *a*-type *Q*-branch shown in Fig. 1 was observed near 1354 cm^{-1}. Using the type of approach described in Ref. (*10*) and the ground state parameters of hydroxylamine (*1*), an approximate set of ν_4 band parameters was calculated from the *Q*-branch data and further low K_- transitions were measured. It was soon clear that transitions with $K_- > 4$ were perturbed. A particularly obvious example of the presence of perturbations is shown in Fig. 2, the ${}^QQ(5)$ branch near 1356 cm^{-1}. Unlike the "normal" ${}^QQ(1)$,

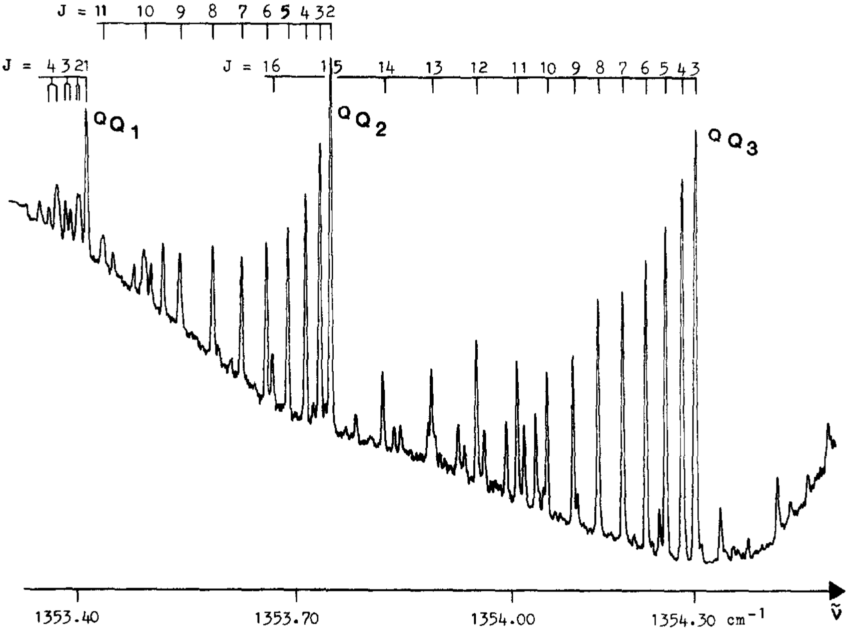

FIG. 1. Examples of unperturbed subbranches: the *a*-type *Q*-branch head of the ν_4 band of hydroxylamine near 1354 cm^{-1}. The *J* assignment is indicated above each absorption line.

${}^{Q}Q(2)$, ${}^{Q}Q(3)$, and ${}^{Q}Q(4)$ subbands which progress from the most intense line ($J = K_-$) toward lower frequency, the ${}^{Q}Q(5)$ starts out toward higher wavenumber and reverses at $J \approx 10$. The ${}^{Q}Q(6)$ (Fig. 3) appears at first sight to be normal, but closer examination shows a discontinuity to be present at $J \approx 11$. Furthermore it soon became clear that transitions with $K_- > 6$ were also perturbed.

In order to be able to progress with this problem, the following procedure was adopted. A set of effective ν_4 band constants were determined from the apparently unperturbed lines with $K_- \leqslant 4$. The first 248 transitions shown in Table I belong to this category; the further 109 ν_4 transitions in this table (marked with an asterisk) all have $K_- > 4$ and are all perturbed.

The analysis of the $K_- \leqslant 4$ data exposed the fact that the *a* and *b* axes are interchanged in the $v_4 = 1$ state relative to their orientation in the ground state; i.e., the magnitude and signs of α^B and α^C are such that the relative magnitudes of I_x and I_y are reversed. This means that in order to adhere to the convention that $B > C$, the representation required in the upper state is I^L and not I^R as in the ground state. This is such a special case that it was not foreseen in the fitting programs used and it was decided to calculate a set of effective parameters for $v_4 = 1$ in which the interchange was *not* taken into account. This has the effect of producing a *C* rotational constant which is larger than *B* and also essentially inverted the labeling of the *K* sublevels in the $v_4 = 1$ state. This is perhaps not a very elegant approach, but since the $v_4 = 1$ state is perturbed and only effective parameters can be determined in any case, it was decided to proceed in this manner.

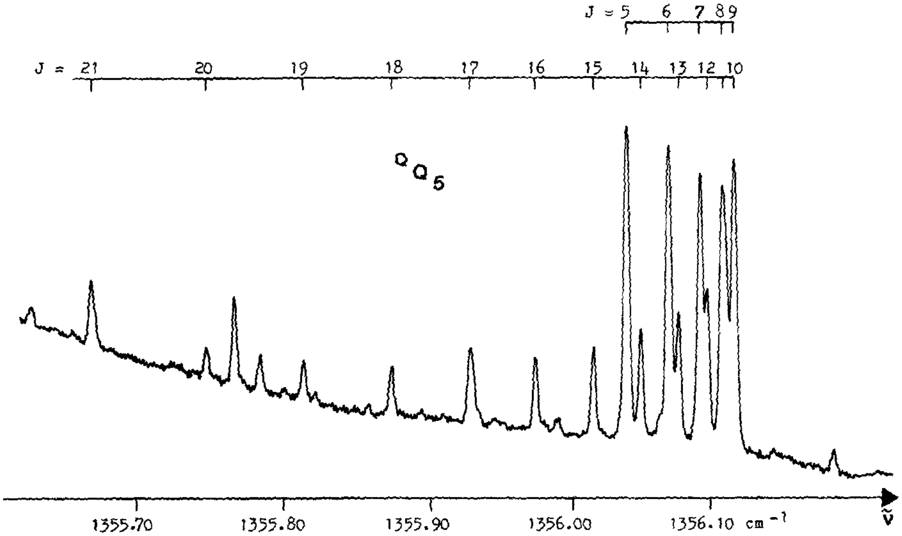

FIG. 2. The strongly perturbed $^{Q}Q_5$ subbranch of the ν_4 band of hydroxylamine. The branch starts out from the most intense transition with $J = K_-$ toward higher wavenumber and doubles back toward lower wavenumber at $J \approx 10$. The energy perturbations causing this behavior are shown in the upper half of Fig. 4.

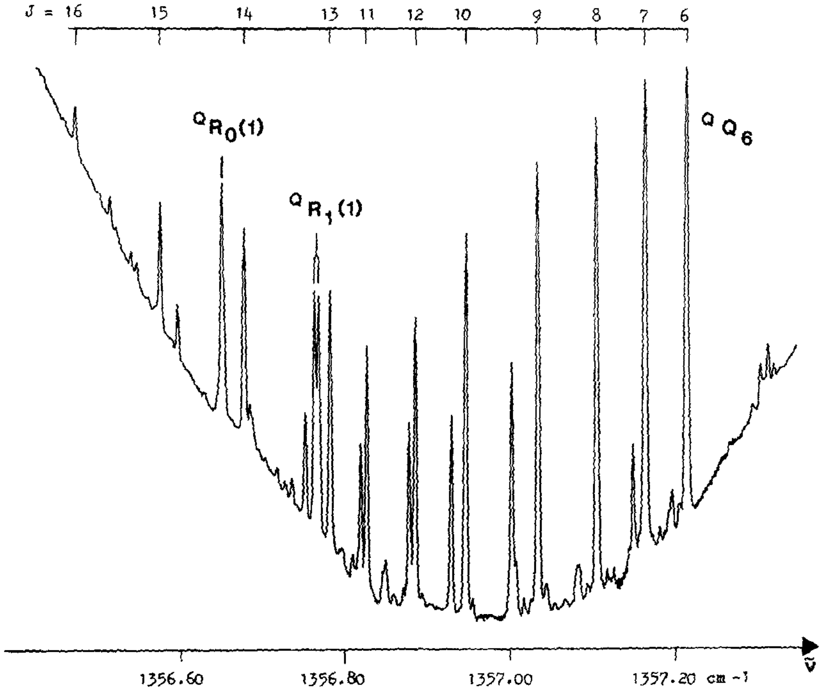

FIG. 3. The $^{Q}Q_6$ subbranch appears at first sight reasonably normal. However, measurement of the relevant P- and R-branch transitions require that the $J = 11$ and $J = 12$ transitions be interchanged relative to the order normally expected. This assignment leads to the "kink" in the $K_- = 6$ plot in Fig. 4.

One of the results of this observation is that we are now able to explain an apparent discrepancy with the perturbation of the $v_5 = 1$ state of hydroxylamine reported earlier from this laboratory (*1*). It is now clear that the *b* and *c* axes are also exchanged in $v_5 = 1$. If this is taken into account it now seems that only the interaction between ν_5 and $3\nu_9$ is of any importance. Once the ν_5 wavenumbers are corrected for this interaction and the magnitude of the *C* rotational constant is allowed to exceed that of the *B* constant, a very adequate fit to the *S*-reduced Watsonian is produced. The effective unperturbed parameters of the ν_5 band calculated by this procedure are included for completeness in Table II.

The effective ν_4 band parameters were calculated from the data of Table I using Watson's *S*-reduced Hamiltonian in the following way. The ground state parameters were constrained at the values given in Ref. (*1*) and all transitions in which $K_- > 4$ in the upper state were given zero weight during the fitting. The results are shown in Table II. As can be seen from the residuals column of Table I, even for transitions with $K_- \leqslant 4$ discrepancies in excess of the estimated accuracy of measurement (0.001 cm^{-1}) are present. However, these are, with a few exceptions, less than 0.01 cm^{-1}. In the case of the transitions with $K_- > 5$ the residuals cover a range of 0.07 to 1.47 cm^{-1}. The deviations of the experimental wavenumbers of these latter transitions from those calculated from the effective parameters of Table II were plotted against $J(J+1)$ (J in $v_4 = 1$). The result is shown in Fig. 4. Under the assumption that the effective parameters reproduce the unperturbed transition frequencies reliably, this plot essentially represents the energy perturbation of the individual $v_4 = 1$ (J, K_-) levels.

As can be seen from Fig. 4, perturbations result in levels with $K_- = 5$ (with the exception of the $J = 5$ level) being pushed upward in energy, whereas levels with higher values of K_- are depressed in energy. Furthermore, with the exception of what appears to be local resonances, for levels with $K_- = 6$, 7, and 8 the plot against $J(J+1)$ is nearly linear, whereas the same plot for $K_- = 5$ shows strong nonlinearity. This behavior can be qualitatively explained by two states interacting with the $v_4 = 1$ state. The energy level scheme proposed is shown in Fig. 5.

The Interactions

The low symmetry of the hydroxylamine molecule (C_s) results in the $v_4 = 1$ state being able to couple with any nearby state. Since ν_4 belongs to the representation A' it can couple with A'' via an *a*-type or *c*-type interaction or with A' via a *b*-type interaction. The *b*- or *c*-type interaction mixes rotational levels of the same J with K_- values differing by ±1; the *a*-type interaction mixes levels with the same J and K_- values. This results in differing resonance characteristics between *b*- and *c*-type interactions on one hand and *a*-type interactions on the other. For a prolate molecule with a large *A* rotational constant, like hydroxylamine, in the former cases the energy separation between the interacting levels changes rapidly with the value of K_-.

For the case of a *b*- or *c*-type interaction between two states, 1 and 2, the energy separation is given approximately by

$$\begin{aligned}\Delta E &= (B_1 - B_2)J(J+1) + \{(A_1 - C_1)(K \pm 1)^2 - (A_2 - C_2)K^2\}\\ &\approx (B_1 - B_2)J(J+1) + (\pm 2K + 1)(A - C),\end{aligned}$$

TABLE I

Transitions of the ν_4 Band of Hydroxylamine (cm^{-1})

J'	K_-'	K_+'	J''	K_-''	K_+''	ν	obs.-calc.	J'	K_-'	K_+'	J''	K_-''	K_+''	ν	obs.-calc.
1	0	1	1	1	1	1347.7688	-0.0070	12	1	11	11	1	10	1373.0741	0.0060
2	0	2	2	1	2	1347.7609	-0.0071	12	1	12	12	0	12	1358.6037	0.0004
2	0	2	1	0	1	1356.6504	-0.0049	13	1	12	12	1	11	1374.6667	0.0069
3	0	3	2	0	2	1358.3137	-0.0068	13	1	13	13	0	13	1358.5471	0.0012
3	0	3	3	1	3	1347.7491	-0.0071	14	1	13	15	0	15	1333.2062	0.0099
4	0	4	3	0	3	1359.9749	-0.0055	14	1	13	13	1	12	1376.2545	0.0104
4	0	4	4	1	4	1347.7344	-0.0061	14	1	13	13	0	13	1381.8734	0.0096
5	0	5	5	1	5	1347.7148	-0.0061	14	1	14	14	0	14	1358.4857	0.0014
6	0	6	6	1	6	1347.6921	-0.0052	14	1	14	13	1	13	1376.5490	0.0014
6	0	6	7	1	6	1335.8830	-0.0051	16	1	15	15	1	14	1379.4041	0.0132
7	0	7	7	1	7	1347.6646	-0.0053	16	1	16	15	1	15	1379.7898	0.0012
7	0	7	8	0	8	1339.7273	-0.0050	16	1	16	16	0	16	1358.3503	0.0020
8	0	8	8	1	8	1347.6344	-0.0041	17	1	17	17	0	17	1358.2768	0.0028
8	0	8	7	0	7	1366.5620	-0.0054	18	1	17	17	1	16	1382.5281	0.0200
9	0	9	10	0	10	1336.2882	-0.0036	18	1	18	17	1	17	1383.0178	0.0051
9	0	9	9	1	9	1347.5996	-0.0036	19	1	19	19	0	19	1358.1172	0.0039
10	0	10	9	0	9	1369.8274	-0.0010	20	1	19	19	1	18	1385.6212	0.0258
10	0	10	10	1	10	1347.5616	-0.0024	20	1	20	19	1	19	1386.2257	0.0060
11	0	11	12	0	12	1332.8332	-0.0008	21	1	21	21	0	21	1357.9422	0.0058
11	0	11	11	1	11	1347.5196	-0.0013	22	1	22	22	0	22	1357.8486	0.0065
12	0	12	11	0	11	1373.0668	-0.0006	23	1	23	23	0	23	1357.7494	0.0055
12	0	12	12	1	12	1347.4734	-0.0005	24	1	24	24	0	24	1357.6491	0.0072
13	0	13	12	1	11	1369.0730	0.0016	24	1	24	23	1	23	1392.5899	0.0087
13	0	13	12	0	12	1374.6797	0.0013	25	1	25	25	0	25	1357.5417	0.0056
13	0	13	13	1	13	1347.4234	0.0005	26	1	26	26	0	26	1357.4335	0.0069
14	0	14	13	0	13	1376.2860	0.0022	2	2	0	2	2	1	1353.7458	0.0048
14	0	14	14	1	14	1347.3698	0.0017	2	2	0	2	1	2	1370.3361	0.0038
15	0	15	15	1	15	1347.3120	0.0027	2	2	1	2	1	1	1370.3296	0.0036
16	0	16	16	1	16	1347.2504	0.0037	3	2	1	2	2	0	1358.7690	0.0026
16	0	16	15	0	15	1379.4810	0.0036	3	2	1	4	2	2	1347.0095	0.0033
17	0	17	17	1	17	1347.1850	0.0049	3	2	1	3	1	3	1370.3242	0.0040
18	0	18	18	1	18	1347.1162	0.0065	3	2	1	3	2	2	1353.7306	0.0044
18	0	18	17	0	17	1382.6560	0.0081	3	2	2	3	1	2	1370.3121	0.0043
19	0	19	19	1	19	1347.0433	0.0080	4	2	2	3	2	1	1360.4304	0.0039
20	0	20	19	0	19	1385.8054	0.0105	4	2	2	4	1	4	1370.3087	0.0046
20	0	20	20	1	20	1346.9662	0.0091	4	2	2	4	2	3	1353.7112	0.0047
21	0	21	20	1	19	1381.6341	0.0096	4	2	3	4	1	3	1370.2880	0.0046
21	0	21	21	1	21	1346.8857	0.0108	5	2	3	5	1	5	1370.2880	0.0040
24	0	24	23	0	23	1392.0341	0.0166	5	2	3	5	2	4	1353.6870	0.0051
25	0	25	24	0	24	1393.5775	0.0194	5	2	4	5	1	4	1370.2575	0.0045
1	1	0	1	1	1	1353.4129	-0.0034	6	2	4	6	2	5	1353.6573	0.0049
1	1	1	1	0	1	1358.9414	-0.0049	6	2	4	6	1	6	1370.2647	0.0049
2	1	1	2	1	2	1353.4038	-0.0035	6	2	4	5	2	3	1363.7347	0.0037
2	1	1	1	1	0	1356.7612	-0.0024	6	2	5	6	1	5	1370.2210	0.0044
2	1	2	2	0	2	1358.9329	-0.0044	7	2	5	7	1	7	1370.2367	0.0051
2	1	2	1	1	1	1356.7657	-0.0033	7	2	5	7	2	6	1353.6223	0.0044
2	1	2	2	1	1	1353.4000	-0.0043	7	2	5	6	1	5	1381.9436	0.0040
3	1	2	3	1	3	1353.3902	-0.0036	7	2	6	7	1	6	1370.1786	0.0045
3	1	2	2	1	1	1358.4223	-0.0028	8	2	6	8	1	8	1370.2044	0.0051
3	1	3	3	1	2	1353.3846	-0.0033	8	2	6	8	2	7	1353.5829	0.0043
3	1	3	2	1	2	1358.4349	-0.0029	8	2	6	7	2	5	1367.0184	0.0041
3	1	3	3	0	3	1358.9195	-0.0043	8	2	7	8	1	7	1370.1286	0.0030
4	1	3	3	1	2	1360.0772	-0.0026	8	2	7	7	2	6	1367.0184	0.0032
4	1	3	4	1	4	1353.3727	-0.0031	9	2	7	9	2	8	1353.5376	0.0032
4	1	4	3	1	3	1360.1000	-0.0031	9	2	7	9	1	9	1370.1681	0.0051
4	1	4	4	0	4	1358.9019	-0.0040	9	2	8	9	1	8	1370.0749	0.0037
4	1	4	4	1	3	1353.3627	-0.0033	10	2	8	10	1	10	1370.1286	0.0060
5	1	4	5	1	5	1353.3507	-0.0027	10	2	8	9	2	7	1370.2805	0.0049
5	1	5	5	0	5	1358.8795	-0.0040	10	2	9	10	1	9	1370.0167	0.0059
5	1	5	5	1	4	1353.3359	-0.0028	10	2	9	9	2	8	1370.2850	0.0070
6	1	5	7	0	7	1347.0732	-0.0017	11	2	9	11	2	10	1353.4354	0.0040
6	1	5	5	0	5	1368.9121	-0.0015	11	2	9	12	2	10	1333.2892	0.0050
6	1	6	5	1	5	1363.4192	-0.0035	11	2	9	11	1	11	1370.0830	0.0048
6	1	6	6	0	6	1358.8527	-0.0040	11	2	10	11	1	10	1369.9461	0.0016
7	1	6	8	1	7	1339.7911	-0.0006	11	2	10	12	2	11	1333.2892	0.0000
7	1	7	7	0	7	1358.8221	-0.0034	11	2	10	11	2	9	1353.4324	0.0013
7	1	7	8	1	8	1339.8936	-0.0030	12	2	10	12	1	12	1370.0341	0.0045
8	1	7	7	1	6	1366.6300	-0.0001	12	2	11	12	1	11	1369.8719	-0.0005
8	1	8	7	1	7	1366.7240	-0.0034	13	2	11	13	1	13	1369.9806	0.0036
8	1	8	8	0	8	1358.7870	-0.0028	13	2	12	13	1	12	1369.7930	-0.0014
9	1	8	10	1	9	1336.3240	0.0013	14	2	12	13	2	11	1376.7322	0.0019
9	1	9	9	0	9	1358.7466	-0.0031	14	2	12	14	1	14	1369.9228	0.0026
9	1	9	10	1	10	1336.4834	-0.0019	14	2	13	14	1	13	1369.7078	-0.0029
10	1	9	9	1	8	1369.8665	0.0032	14	2	13	13	2	12	1376.7322	-0.0072
10	1	10	9	1	9	1370.0169	0.0002	15	2	13	15	1	15	1369.8604	0.0010
10	1	10	10	0	10	1358.7042	-0.0011	15	2	14	15	1	14	1369.6120	-0.0092
11	1	10	12	1	11	1332.8332	0.0031	16	2	14	15	2	13	1379.9203	-0.0019
11	1	11	12	1	12	1333.0622	-0.0008	16	2	14	16	1	16	1369.7930	-0.0014
11	1	11	11	0	11	1358.6556	-0.0009	16	2	15	15	2	14	1379.9203	-0.0176

* Zero weight in the fit.

TABLE I—*Continued*

J'	K_-'	K_+'	J''	K_-''	K_+''	ν	obs.-calc.
17	2	15	17	1	17	1369.7217	-0.0035
17	2	16	17	1	16	1369.4045	-0.0208
18	2	16	17	2	15	1383.0864	-0.0032
18	2	17	17	2	16	1383.0833	-0.0314
18	2	17	18	1	17	1369.2909	-0.0281
19	2	17	19	1	19	1369.5624	-0.0120
19	2	18	19	1	18	1369.1691	-0.0381
20	2	18	19	2	17	1386.2143	-0.0175
20	2	18	20	1	20	1369.4761	-0.0166
20	2	19	19	2	18	1386.2205	-0.0496
20	2	19	20	1	19	1369.0416	-0.0484
21	2	19	21	1	21	1369.3830	-0.0238
22	2	20	22	1	22	1369.2847	-0.0320
23	2	21	23	1	23	1369.1805	-0.0418
3	3	1	3	3	0	1354.2979	0.0063
3	3	1	4	3	2	1347.5775	0.0050
3	3	1	3	2	1	1381.9391	0.0060
4	3	2	4	3	1	1354.2783	0.0060
4	3	2	4	2	2	1381.9186	0.0057
5	3	3	5	3	2	1354.2546	0.0064
5	3	3	5	2	3	1381.8931	0.0054
6	3	3	6	3	4	1354.2261	0.0069
6	3	3	7	2	5	1370.1060	0.0065
6	3	4	6	2	4	1381.8635	0.0062
6	3	4	7	2	6	1370.1060	0.0061
7	3	5	8	3	6	1340.7562	0.0051
7	3	5	7	3	4	1354.1911	0.0056
7	3	5	6	3	4	1365.9458	0.0042
7	3	5	7	2	5	1381.8274	0.0055
8	3	6	8	2	6	1381.7868	0.0053
8	3	6	7	3	5	1367.5860	0.0047
8	3	6	8	3	5	1354.1528	0.0059
9	3	6	9	3	7	1354.1099	0.0063
9	3	6	8	3	5	1369.2222	0.0065
9	3	7	9	2	7	1381.7410	0.0051
10	3	8	10	2	8	1381.6899	0.0046
10	3	8	10	3	7	1354.0616	0.0061
11	3	9	11	3	8	1354.0076	0.0050
11	3	9	11	2	9	1381.6341	0.0045
12	3	9	12	3	10	1353.9499	0.0050
13	3	10	13	3	11	1353.8860	0.0035
13	3	10	12	3	9	1375.7020	0.0024
14	3	11	14	3	12	1353.8174	0.0020
15	3	12	14	3	11	1378.9088	0.0002
16	3	13	16	3	14	1353.6653	-0.0017
4	4	1	4	3	1	1393.7521	-0.0128
4	4	1	4	4	0	1355.0649	-0.0132
5	4	2	5	3	2	1393.7282	-0.0117
5	4	2	5	4	1	1355.0430	-0.0116
6	4	3	6	3	3	1393.7009	-0.0091
6	4	3	6	4	2	1355.0164	-0.0101
7	4	4	7	3	4	1393.6672	-0.0078
7	4	4	6	4	3	1366.7365	-0.0112
7	4	4	7	4	3	1354.9845	-0.0092
8	4	5	9	4	6	1339.8383	-0.0086
8	4	5	8	3	5	1393.6285	-0.0066
8	4	5	8	4	4	1354.9494	-0.0069
9	4	6	9	4	5	1354.9090	-0.0051
9	4	6	9	3	6	1393.5863	-0.0039
9	4	6	8	4	5	1370.0169	-0.0066
10	4	7	10	3	7	1393.5376	-0.0027
10	4	7	11	4	8	1336.3993	-0.0055
11	4	8	11	3	8	1393.4849	-0.0006
11	4	8	10	4	7	1373.2757	-0.0028
12	4	9	12	3	9	1393.4263	0.0006
12	4	9	13	4	10	1332.9459	-0.0010
13	4	10	13	4	9	1354.7006	0.0013
13	4	10	13	3	10	1393.3635	0.0024
13	4	10	12	4	9	1376.5134	0.0010
13	4	10	14	3	12	1369.8719	0.0023
14	4	11	14	4	10	1354.6367	0.0026
14	4	11	14	3	11	1393.2974	0.0059
15	4	12	14	4	11	1379.7269	0.0022
15	4	12	15	3	12	1393.2219	0.0049
15	4	12	15	4	11	1354.5686	0.0043
16	4	13	16	4	12	1354.4952	0.0053
16	4	13	16	3	13	1393.1434	0.0057
17	4	14	16	5	12	1333.2451	0.0029
17	4	14	17	3	14	1393.0604	0.0069
17	4	14	16	4	13	1382.9214	0.0062
17	4	14	17	4	13	1354.4168	0.0058
18	4	15	18	3	15	1392.9707	0.0063
18	4	15	18	4	14	1354.3337	0.0062
19	4	16	19	4	15	1354.2461	0.0065
19	4	16	19	3	16	1392.8765	0.0060
19	4	16	18	4	15	1386.0892	0.0058
20	4	17	20	3	17	1392.7782	0.0063
20	4	17	20	4	16	1354.1536	0.0065
21	4	18	21	3	18	1392.6733	0.0049
22	4	19	22	3	19	1392.5638	0.0037
5	5	0	5	5	1	1356.0392	-0.0757*
6	5	1	5	5	0	1366.1436	-0.0175*
6	5	1	6	5	2	1356.0689	-0.0189*
7	5	3	7	5	2	1356.0919	0.0356*
8	5	3	7	5	2	1369.5368	0.0879*
8	5	3	8	5	4	1356.1072	0.0870*
8	5	3	9	5	4	1341.0012	0.0868*
9	5	4	9	5	5	1356.1156	0.1360*
9	5	4	10	5	5	1339.3320	0.1346*
10	5	5	9	5	4	1372.8982	0.1813*
10	5	5	10	5	6	1356.1156	0.1810*
11	5	6	11	5	7	1356.1092	0.2241*
11	5	6	12	5	7	1335.9768	0.2251*
11	5	6	10	5	5	1374.5689	0.2256*
12	5	7	11	5	6	1376.2310	0.2664*
12	5	7	12	5	8	1356.0967	0.2655*
13	5	8	13	5	9	1356.0765	0.3036*
13	5	8	14	5	9	1332.5946	0.3034*
14	5	9	14	5	10	1356.0495	0.3394*
14	5	9	13	5	8	1379.5311	0.3394*
15	5	11	15	5	10	1356.0155	0.3726*
16	5	11	15	5	10	1382.8030	0.4052*
16	5	11	16	5	12	1355.9753	0.4040*
17	5	13	17	5	12	1355.9279	0.4325*
18	5	13	18	5	14	1355.8730	0.4579*
18	5	13	17	5	12	1386.0416	0.4591*
19	5	14	18	5	13	1387.6479	0.4812*
19	5	14	19	5	15	1355.8125	0.4821*
20	5	15	21	4	17	1370.2114	0.5053*
20	5	15	20	5	16	1355.7448	0.5033*
21	5	17	21	5	16	1355.6671	0.5189*
22	5	17	22	5	18	1355.5886	0.5379*
22	5	17	21	5	16	1392.4267	0.5402*
23	5	19	23	5	18	1355.5003	0.5513*
24	5	20	24	5	19	1355.4060	0.5630*
25	5	21	25	5	20	1355.3087	0.5758*
26	5	22	26	5	21	1355.1986	0.5800*
6	6	0	6	6	1	1357.2127	-0.2080*
7	6	1	7	6	2	1357.1633	-0.2274*
7	6	1	6	6	0	1368.9121	-0.2264*
8	6	3	8	6	2	1357.1043	-0.2520*
9	6	3	10	6	4	1340.2553	-0.2849*
9	6	3	9	6	4	1357.0347	-0.2830*
10	6	5	10	6	4	1356.9476	-0.3272*
11	6	6	11	6	5	1356.8250	-0.4027*
12	6	6	11	6	5	1377.0123	-0.2916*
12	6	6	12	6	7	1356.8846	-0.2917*
13	6	7	13	6	8	1356.7802	-0.3405*
13	6	7	14	6	8	1333.3050	-0.3409*
14	6	8	14	6	9	1356.6760	-0.3849*
14	6	8	13	6	7	1380.1497	-0.3860*
15	6	9	15	6	10	1356.5680	-0.4289*
15	6	9	14	6	8	1381.7138	-0.4303*
16	6	10	16	6	11	1356.4545	-0.4743*
16	6	10	15	6	9	1383.2742	-0.4732*
17	6	12	17	6	11	1356.3347	-0.5217*
18	6	12	18	6	13	1356.2069	-0.5731*
18	6	12	17	6	11	1386.3657	-0.5729*
19	6	14	19	6	13	1356.0689	-0.6305*
20	6	15	20	6	14	1355.9270	-0.6877*
21	6	16	21	6	15	1355.7814	-0.7446*
22	6	16	22	6	17	1355.6234	-0.8098*
22	6	16	21	6	15	1392.4502	-0.8080*
23	6	18	23	6	17	1355.4579	-0.8785*
24	6	19	24	6	18	1355.2857	-0.9498*
7	7	0	7	7	1	1358.5827	-0.4357*
8	7	2	8	7	1	1358.5295	-0.4565*
9	7	3	9	7	2	1358.4693	-0.4804*
10	7	3	10	7	4	1358.4019	-0.5074*
10	7	3	11	7	4	1339.9548	-0.5080*
11	7	4	11	7	5	1358.3269	-0.5380*
11	7	4	10	7	3	1376.7739	-0.5376*
12	7	5	12	7	6	1358.2440	-0.5726*
12	7	5	13	7	6	1336.4496	-0.5729*
13	7	6	12	7	5	1379.9463	-0.6121*
13	7	6	13	7	7	1358.1524	-0.6119*
14	7	7	13	7	6	1381.5161	-0.6587*
14	7	7	14	7	8	1358.0497	-0.6583*
14	7	7	15	7	8	1332.9107	-0.6587*
15	7	8	14	7	7	1383.0698	-0.7166*

TABLE I—*Continued*

J'	K_-'	K_+'	J"	K_-"	K_+"	ν	obs.-calc.	J'	K_-'	K_+'	J"	K_-"	K_+"	ν	obs.-calc.
15	7	8	15	7	9	1357.9293	-0.7185*	14	8	6	13	8	5	1383.1439	-0.9904*
16	7	10	16	7	9	1357.7717	-0.8120*	14	8	6	14	8	7	1359.6845	-0.9923*
17	7	10	17	7	11	1357.6074	-0.9083*	15	8	7	16	8	8	1332.7870	-1.0350*
17	7	10	16	7	9	1386.0892	-0.9059*	15	8	7	15	8	8	1359.5877	-1.0333*
8	8	0	8	8	1	1360.1299	-0.8048*	16	8	8	16	8	9	1359.4838	-1.0777*
9	8	1	9	8	2	1360.0722	-0.8288*	16	8	8	15	8	7	1386.2830	-1.0774*
10	8	2	9	8	1	1376.7739	-0.8547*	17	8	10	17	8	9	1359.3740	-1.1244*
10	8	2	10	8	3	1360.0083	-0.8552*	18	8	11	18	8	10	1359.2569	-1.1748*
11	8	3	11	8	4	1359.9362	-0.8862*	19	8	12	19	8	11	1359.1340	-1.2275*
11	8	3	12	8	4	1339.8229	-0.8867*	20	8	12	20	8	13	1359.0039	-1.2838*
12	8	4	11	8	3	1379.9709	-0.9194*	20	8	12	19	8	11	1392.4743	-1.2829*
12	8	4	12	8	5	1359.8590	-0.9185*	21	8	14	21	8	13	1358.8643	-1.3460*
13	8	5	13	8	6	1359.7744	-0.9546*	22	8	15	22	8	14	1358.7224	-1.4071*
13	8	5	14	8	6	1336.3163	-0.9552*	23	8	16	23	8	15	1358.5731	-1.4720*
13	8	5	12	8	4	1381.5596	-0.9549*								

where $K = K_-$ and it is assumed that $(A_1 - C_1) \approx (A_2 - C_2) \approx (A - C)$. Consequently a relatively sharp resonant dependence on K_- is observed with one pair of levels probably displaying a much stronger interaction than all others.

For the *a*-type interaction the separation between the mixing levels changes much more slowly with K_-:

$$\Delta E \approx (B_1 - B_2)J(J + 1) + \{(A_1 - C_1) - (A_2 - C_2)\}K^2.$$

This results in a slow buildup or recession of resonance. At resonance a sharp change in the sign of the energy shift occurs.

c-Type Interaction between $v_4 = 1$ and ($v_6 = 1$; $v_9 = 1$)

The band origin of ν_4 is approximately 1353.3 cm^{-1} and a weak band at 1297 cm^{-1} was assigned by Giguere and Liu (*2*) as the combination band $\nu_6 + \nu_9$. Any interaction between these two modes would be expected to be of high order and consequently produce only significant energy shifts under conditions of near resonance. Accurate band parameters for both ν_6 and ν_9 have been determined in our previous work (*1*). Consequently approximate constants for the combination state ($v_6 = 1$; $v_9 = 1$) can

TABLE II
Band Parameters* of NH_2OH

Parameter		Ground State^a	$v_4 = 1^b$	$v_5 = 1^{b,c}$
ν_0	[cm^{-1}]	0.0	1353.309(1)	1115.4702(2)
A	[GHz]	190.9766(2)	194.22(1)	191.3616(4)
B	[GHz]	25.21875(2)	25.0964(4)	25.10341(9)
C	[GHz]	25.15659(2)	25.1289(5)	25.10916(9)
D_J	[MHz]	0.0757(3)	0.0743(6)	0.0761(8)
D_{JK}	[MHz]	0.661(5)	0.37(2)	0.748(1)
D_K	[MHz]	3.583(41)	1.3(6)	3.873(4)
d_1	[kHz]	-1.08(8)	-1.08^a	-1.08^a
d_2	[kHz]	1.58(9)	1.8(4)	1.4(2)

*= S-reduced Watsonian, a= constrained at these values from Ref.(*1*).
b= effective values with axis inversion not taken into account.
c= effective values obtained from data set of Ref. (*1*) corrected for the Coriolis interaction with v_9=3.

TABLE III

Energy Separation* between Levels of $v_4 = 1$ and ($v_6 = 1$; $v_9 = 1$) (in cm^{-1})

$v_4=1$	$(v_6=1;v_9=1)$	J = min	J = 20
$K_-= 6$	$K_-= 7$	-8.39	-3.92
$K_-= 5$	$K_-= 6$	0.56	4.63
$K_-= 4$	$K_-= 5$	9.90	14.05

* $v_4=1$ - $(v_6=1;v_9=1)$ based on parameters given in text.

be calculated. The following values for the rotational constants were obtained: $A = 189.164$ GHz, $B = 24.895$ GHz, and $C = 24.713$ GHz. Assuming the distortion parameters of ($v_6 = 1$; $v_9 = 1$) to be equal to those of the ground state (*1*) and the ν_6

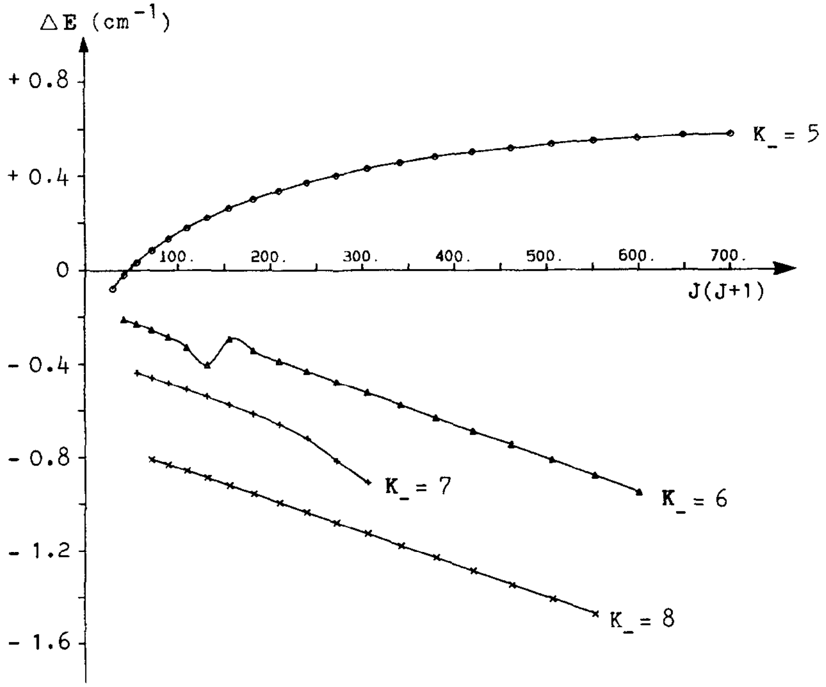

FIG. 4. A plot of the ν_4 band residuals of Table I (observed − calculated) for the transitions with $K_- = 5$, 6, 7, 8 against $J(J+1)$, where J is the upper state value. These transitions were given zero weight in the fit to determine the $v_4 = 1$ effective parameters (Table II). Consequently, provided the $v_4 = 1$ levels with $K_- \leqslant 4$ are free of perturbation, this is effectively a plot of energy level perturbation against $J(J+1)$. As can be seen the $K_- = 5$ levels are displaced upward in energy with a strong nonlinearity in the plot. Some of the transitions yielding the data plotted here are shown in Fig. 2. The $K_- = 6, 7, 8$ levels are displaced downward in energy and the plot is generally linear. Some of the transitions corresponding to the $K_- = 6$ plot are shown in Fig. 3. The "kink" at $J \approx 12$ is produced by the assignments shown in Fig. 3. It is worthy of note that the first point on the $K_- = 5$ plot, i.e., $J = 5$, is also negatively displaced. This is an indication of the correctness of our treatment since this level has no interaction partner in the c-type Coriolis between $v_4 = 1$ and ($v_6 = 1$; $v_9 = 1$) (see text and Fig. 5).

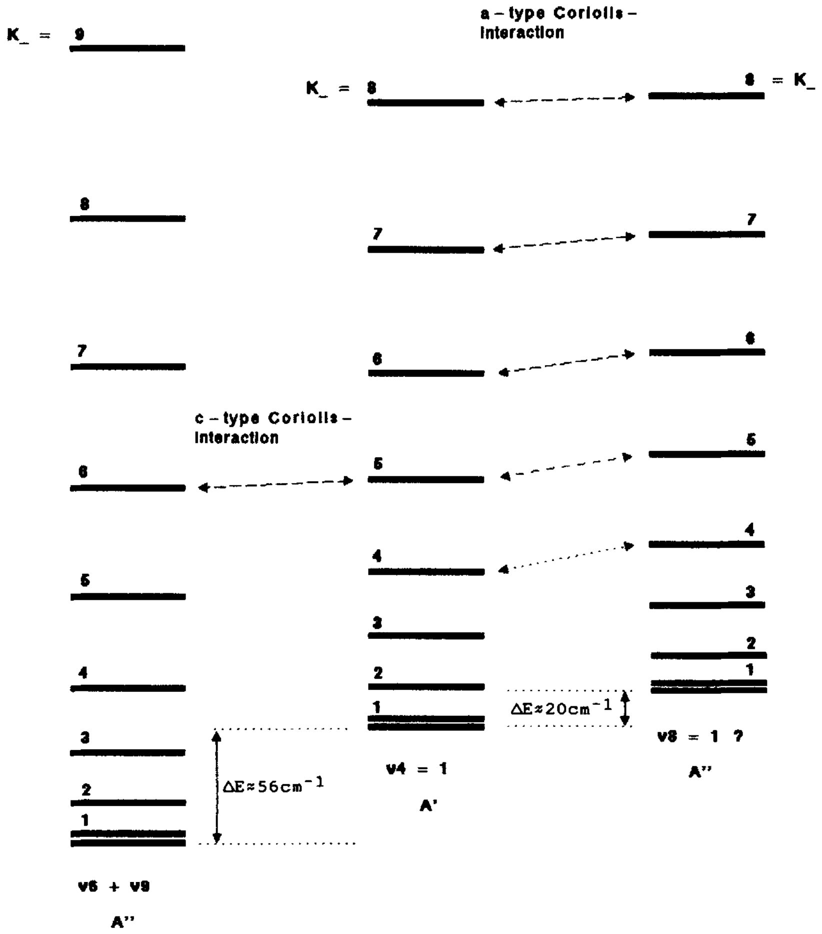

FIG. 5. Energy level scheme proposed to explain the perturbations shown in Figs. 2, 3, and 4. A near resonance between $K_- = 6$ levels of the ($v_6 = 1$; $v_9 = 1$) combination state and $K_- = 5$ levels of $v_4 = 1$ explains the strong perturbation of ν_4 transitions with $K_- = 5$ in the upper state which is shown in Figs. 2 and 5. This is indicated here as a *c*-type Coriolis interaction (because of axis switching, the designation as *b*- or *c*-type interaction becomes somewhat ambiguous). The perturbations observed for transitions with $K_- > 5$ is explained by the presence of a second nearby state which undergoes an *a*-type ($\Delta K_- = 0$) interaction with $v_4 = 1$. This state would need to be of the order of 20 cm^{-1} above $v_4 = 1$ to explain the observations qualitatively. Since there is no other possibility, it is proposed that the band concerned is the still unobserved fundamental ν_8 (see text).

$+ \nu_9$ band origin to be 1297 cm^{-1}, a close resonance between $K_- = 6$ levels of ($v_6 = 1$; $v_9 = 1$) and the $K_- = 5$ levels of $v_4 = 1$ is to be expected, as shown in Fig. 5. The energy separation between the various K_- levels of these two states for extremes of J are shown in Table III. As can be seen, based on this calculation, the $J = 6$, $K_- = 6$ level of ($v_6 = 1$; $v_9 = 1$) is only 0.56 cm^{-1} below the $J = 6$, $K_- = 5$ level of $v_4 = 1$. The separation between levels increases with rising J values and reaches 4.6 cm^{-1} at $J = 20$. Thus, the observed strong positive perturbation of the $K_- = 5$ levels of

$v_4 = 1$ can be qualitatively explained by the c-type interaction expected between these two modes and the close resonance with the $K_- = 6$ levels of $(v_6 = 1; v_9 = 1)$.

The closest approach between a $K_- = 5$ level of $(v_6 = 1; v_9 = 1)$ and a $K_- = 4$ level of $v_4 = 1$ is 9.89 cm^{-1} (Table III), thus explaining the lack of any pronounced perturbation in the $K_- = 4$ $v_4 = 1$ levels. Nevertheless a small upward energy shift might be expected from this source.

For all $v_4 = 1$ levels with $K_- \leqslant 5$ there is a tendency for this c-type interaction to cause a slight reduction in energy. On the other hand the a-type component of this $A' \leftrightarrow A''$ interaction would tend to cause a positive energy shift. However, as can be seen from energy differences between the relevant levels in Fig. 5 it would seem that the a-type component is of little importance.

A question arising out of the treatment carried out here is, how good is the approximation that the $v_4 = 1$ levels with $K_- < 5$ are not perturbed? A close examination of Table I reveals that in general the residuals tend to increase with increasing J. There is a definite systematic deviation for transitions involving the $J_{1,(J-1)}$ and $J_{2,(J-1)}$ $v_4 = 1$ levels whereas transitions to the other $K_- = 1$ or $K_- = 2$ level fit reasonably well. This shows, as would be expected, that these levels are *not* completely free from the effects of the interactions. Nevertheless we are confident that the effective constants of Table II reproduce the unperturbed spectrum reasonably accurately.

a-Type Interaction between $v_4 = 1$ and $v_8 = 1$

The $v_4 = 1$ levels with $K_- > 4$ display a smoothly increasing negative deviation from the unperturbed energies (Fig. 5). This type of behavior could be explained by an a-type interaction between $v_4 = 1$ and a nearby state. Unfortunately there is no direct evidence for the existence of such a state. However, it is now well established (*1*, *11*) that Giguere and Liu (*2*) misassigned the overtone of the torsional motion as ν_8, the weak band of the NH_2 rocking motion. So far there is still no experimental information on this band, but an ab initio calculation (*12*) has positioned it at 1451 cm^{-1}. Bearing in mind that ab initio calculations usually overestimate vibrational frequencies, ν_8 is probably to be expected in the range 1350–1400 cm^{-1}. We estimate that the perturbations observed in ν_4 would be qualitatively reproduced if the $v_8 = 1$ state was approximately 20 cm^{-1} above $v_4 = 1$, i.e., near 1375 cm^{-1}. The ν_8 band is expected to be very weak (*12*). A search of the region with our diode laser spectrometer did not allow the spectrum to be assigned. However, the problem here is the same as with our attempts to observe the combination band $\nu_6 + \nu_9$, namely it is difficult to assign a weak spectrum in the presence of a very much stronger one.

It appears that there are also several very localized perturbations present in the ν_4 spectrum. One obvious example is present in the $K_- = 6$ levels and this shows itself near $J = 10$ as the sharp feature in Fig. 4 and in the irregular numbering of the transitions of the ${}^QQ_6$ in Fig. 3. At present we have no explanation of this effect which, because of its sharp resonant nature, is presumably caused by a b- or c-type interaction. We are however confident that the effect is real since the points in Fig. 4 correspond to the residual of at least two transition wavenumbers, i.e., a Q-branch and either a P- or an R-branch transition (Table I).

In view of the lack of detailed information on $\nu_6 + \nu_9$ or ν_8 it is impossible to carry out further analysis of the perturbation at the moment. Obviously, we could calculate empirical correction parameters as in Ref. (*1*), but it is questionable if this is of any more value than a simple extrapolation of the residuals of Table I.

Despite the fact that we have been unable to carry out a full analysis of the perturbations observed in this work, it is nevertheless gratifying that we were able to piece together so much of the strongly perturbed ν_4 spectrum.

Deuterated Hydroxylamine

Fairly good rotational constants for all five deuterated forms of hydroxylamine in the ground state were available at the beginning of this investigation from the microwave work of Tsunekawa (*13*). It appears, however, that the only previous infrared study of deuterated hydroxylamine was carried out on a solid state sample of ND_2OD (*14*). These data appear to be not very reliable as a guide for the gas-phase spectra since the data obtained for NH_2OH in the solid state (*14*) differed considerably and moreover, apparently unpredictably, from the gas-phase results.

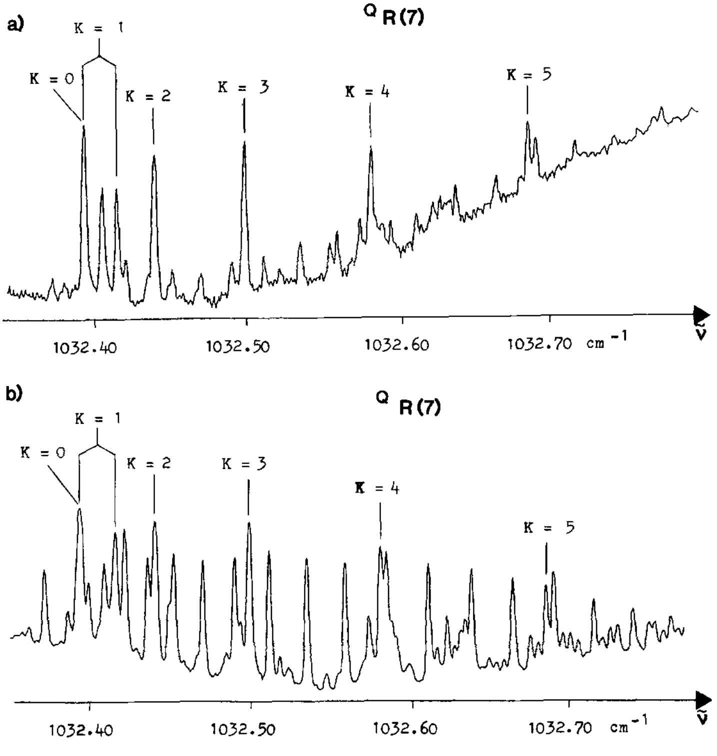

FIG. 6. A section of the spectrum of a deuterated sample of hydroxylamine near 1032 cm^{-1} showing (a) the effects of adding vapor from a 1:1 H_2O/D_2O mixture and (b) from a 99% D_2O sample. The assigned transitions, ${}^{Q}R(7)$ with K_- as indicated, belong to the ν_5 band of NHDOD. The lines which appear between the NHDOD transitions at high deuterium concentrations (b) presumably belong to an unidentified band of ND_2OD.

Since the exchange of all three hydrogen atoms occurs so readily the only deuterated form which can in principle be prepared with high purity is ND_2OD. Work was initiated with the aim of measuring the ν_4 band of the fully deuterated form. In this case this band would not be expected to show the same perturbations as observed in normal hydroxylamine.

In the solid state, ν_4 was assigned to a band at 942 cm^{-1} (*14*). The range 900–1050 cm^{-1} was searched using our fully deuterated sample in a White cell which had been treated with 99% D_2O. A typical *a*-type, near prolate rotor *Q*-branch system was ob-

TABLE IV

Transitions of the ν_5 Band of NHDOD (cm^{-1})

J'	K_-'	K_+'	J''	K_-''	K_+''	ν	obs.-calc.
4	0	4	5	0	5	1013.3909	-0.0001
6	0	6	5	0	5	1029.4962	-0.0014
7	0	7	6	0	6	1030.9483	0.0015
7	0	7	8	0	8	1008.9596	0.0020
8	0	8	7	0	7	1032.3948	0.0012
9	0	9	8	0	8	1033.8393	0.0009
13	0	13	12	0	12	1039.6022	0.0006
14	0	14	13	0	13	1041.0392	-0.0008
17	0	17	16	0	16	1045.3559	0.0004
4	1	4	5	1	5	1013.4787	-0.0003
4	1	3	5	1	4	1013.3233	0.0001
6	1	6	5	1	5	1029.5002	-0.0016
6	1	5	5	1	4	1029.5151	-0.0025
7	1	7	8	1	8	1009.1182	0.0027
7	1	6	6	1	5	1030.9600	0.0013
7	1	7	6	1	6	1030.9600	0.0015
7	1	6	8	1	7	1008.8048	0.0008
8	1	7	7	1	6	1032.3948	0.0002
8	1	8	7	1	7	1032.4157	0.0006
9	1	8	8	1	7	1033.8255	0.0003
9	1	9	8	1	8	1033.8728	0.0012
13	1	12	12	1	11	1039.4970	0.0013
13	1	13	12	1	12	1039.6989	0.0012
14	1	14	13	1	13	1041.1538	-0.0006
14	1	13	13	1	12	1040.9008	0.0001
17	1	16	16	1	15	1045.0892	0.0022
17	1	17	16	1	16	1045.5256	-0.0003
4	2	3	5	2	4	1013.4357	-0.0013
4	2	2	5	2	3	1013.4357	0.0013
6	2	5	5	2	4	1029.5434	-0.0017
6	2	4	5	2	3	1029.5434	-0.0022
7	2	6	8	2	7	1008.9963	0.0012
7	2	5	6	2	4	1030.9949	0.0007
7	2	6	6	2	5	1030.9949	0.0009
7	2	5	8	2	6	1008.9837	0.0020
8	2	6	7	2	5	1032.4400	0.0005
8	2	7	7	2	6	1032.4400	-0.0001
9	2	8	8	2	7	1033.8843	0.0008
9	2	7	8	2	6	1033.8817	0.0002
13	2	12	12	2	11	1039.6319	0.0018
13	2	11	12	2	10	1039.6074	-0.0015
14	2	12	13	2	11	1041.0265	-0.0024
14	2	13	13	2	12	1041.0611	0.0011
17	2	15	16	2	14	1045.2518	-0.0030
17	2	16	16	2	15	1045.3387	0.0043
4	3	1	5	3	2	1013.4948	-0.0013
6	3	3	5	3	2	1029.6020	-0.0021
7	3	4	6	3	3	1031.0538	0.0009
7	3	4	8	3	5	1009.0538	0.0019
8	3	5	7	3	4	1032.4986	-0.0003
9	3	6	8	3	5	1033.9418	-0.0002
13	3	10	12	3	9	1039.6837	0.0001
14	3	11	13	3	10	1041.1096	-0.0012
14	3	12	13	3	11	1041.1096	-0.0019
17	3	15	16	3	14	1045.3732	-0.0001
17	3	14	16	3	13	1045.3699	-0.0005
4	4	0	5	4	1	1013.5787	-0.0007
7	4	3	6	4	2	1031.1355	0.0008
7	4	3	8	4	4	1009.1390	0.0018
8	4	4	7	4	3	1032.5806	-0.0003
9	4	5	8	4	4	1034.0229	-0.0014
13	4	9	12	4	8	1039.7679	-0.0005
14	4	10	13	4	9	1041.1936	-0.0031
17	4	13	16	4	12	1045.4603	-0.0015
5	5	1	5	5	0	1021.0025	-0.0032
6	5	2	6	5	1	1020.9886	-0.0028
7	5	2	8	5	3	1009.2471	0.0020
7	5	3	7	5	2	1020.9721	-0.0026
7	5	2	6	5	1	1031.2395	0.0007
8	5	4	8	5	3	1020.9536	-0.0020
8	5	3	7	5	2	1032.6853	0.0000
9	5	5	9	5	4	1020.9333	-0.0008
9	5	4	8	5	3	1034.1278	-0.0012
13	5	8	12	5	7	1039.8736	-0.0018
14	5	9	13	5	8	1041.3015	-0.0030
17	5	12	16	5	11	1045.5708	-0.0022
6	6	1	6	6	0	1021.1174	-0.0011
7	6	1	8	6	2	1009.3767	0.0016
7	6	2	7	6	1	1021.1020	-0.0004
8	6	3	8	6	2	1021.0835	-0.0005
9	6	4	9	6	3	1021.0626	-0.0007
9	6	3	8	6	2	1034.2544	-0.0012
10	6	5	10	6	4	1021.0391	-0.0010
11	6	6	11	6	5	1021.0137	-0.0010
13	6	7	12	6	6	1040.0022	-0.0026
17	6	11	16	6	10	1045.7139	0.0067
7	7	1	7	7	0	1021.2518	0.0007
8	7	2	8	7	1	1021.2347	0.0011
9	7	3	9	7	2	1021.2150	0.0012
9	7	2	8	7	1	1034.4028	-0.0003
10	7	4	10	7	3	1021.1927	0.0008
11	7	5	11	7	4	1021.1694	0.0017
12	7	6	12	7	5	1021.1417	0.0005
13	7	7	13	7	6	1021.1127	0.0003
14	7	8	14	7	7	1021.0805	-0.0009
8	8	1	8	8	0	1021.4044	0.0011
9	8	2	9	8	1	1021.3863	0.0014
10	8	3	10	8	2	1021.3667	0.0023
11	8	4	11	8	3	1021.3441	0.0023
12	8	5	12	8	4	1021.3183	0.0012
13	8	6	13	8	5	1021.2910	0.0006
14	8	7	14	8	6	1021.2621	0.0007
15	8	8	15	8	7	1021.2298	-0.0006
9	9	1	9	9	0	1021.5758	0.0006
10	9	2	10	9	1	1021.5577	0.0011
11	9	3	11	9	2	1021.5374	0.0012
12	9	4	12	9	3	1021.5145	0.0007
13	9	5	13	9	4	1021.4906	0.0011
14	9	6	14	9	5	1021.4635	0.0002
15	9	7	15	9	6	1021.4340	-0.0012
10	10	1	10	10	0	1021.7669	-0.0005
11	10	2	11	10	1	1021.7491	-0.0005
12	10	3	12	10	2	1021.7297	-0.0005
13	10	4	13	10	3	1021.7092	0.0001
14	10	5	14	10	4	1021.6856	-0.0008
15	10	6	15	10	5	1021.6611	-0.0008
16	10	7	16	10	6	1021.6352	-0.0006
17	10	8	17	10	7	1021.6061	-0.0018
11	11	1	11	11	0	1021.9775	-0.0035
12	11	2	12	11	1	1021.9641	-0.0012
13	11	3	13	11	2	1021.9482	0.0000
14	11	4	14	11	3	1021.9310	0.0013
15	11	5	15	11	4	1021.9117	0.0018
16	11	6	16	11	5	1021.8906	0.0019
17	11	7	17	11	6	1021.8654	-0.0007

served near 1021 cm^{-1} and by using the usual assignment techniques, some of the associated *P* and *R* branches were located and measured. The $^{Q}R(7)$ region is shown in Fig. 6.

It soon became clear that these lines did not originate from the fully deuterated form of hydroxylamine. They were most intense when a small quantity of the vapor from a 1:1 mixture of D_2O/H_2O was also admitted into the cell (Fig. 6a). Addition of 99% D_2O tended to reduce the strength of these lines and simultaneously caused other lines (presumably from the fully deuterated species) to increase in intensity (Fig. 6b). This showed that the spectrum which had been assigned originated from a partially deuterated form of hydroxylamine. The wavenumbers of the transitions measured are shown in Table IV.

The problem now was to identify which of the four possible partially deuterated species gave rise to this spectrum. Since the rotational constants of hydroxylamine are very large only four ground state microwave transitions had been measured for each deuterated species (*13*). With the ground state centrifugal distortion parameters constrained at the values determined for NH_2OH (*1*), a fit of the data of Table IV combined with successive microwave data sets from each isotopic species was carried out. This procedure showed quite definitely that the spectrum originated from NHDOD. The experimental data (microwave (*13*) and infrared) were then fit to the *S*-reduced Watsonian. The band parameters determined are shown in Table V.

The only problem remaining was the band assignment. In NH_2OH, the most intense band is ν_5, the NH_2 wag, near 1187 cm^{-1}. From a comparison of the NH_2OH (*2*) and ND_2OD solid state data (*14*), ν_5 seemed to be the most likely assignment in this case. This view is strongly supported by comparison of the rovibrational interaction coefficients (α's) obtained here, those obtained for ν_5 in NH_2OH (*1*), and those obtained in this work for ν_4. The relevant data are gathered together in Table VI.

TABLE V

The Effective Parameters of the ν_5 Band of NHDOD

Parameter		Ground State	$v_5 = 1$
ν_0	[cm-1]	0.0	1020.7488(6)
A	[GHz]	124.2522[a]	124.571(1)[b]
B	[GHz]	22.30489(4)	22.1896(3)
C	[GHz]	21.68113(4)	21.7214(3)
D_J	[MHz]	0.051(4)	0.051(3)
D_{JK}	[MHz]	0.38(2)	0.31(2)
D_K	[MHz]	3.583[c]	3.835(9)
d_1	[kHz]	-1.08[c]	-1.08[c]
d_2	[kHz]	1.58[c]	1.58[c]
H_{KJ}	[kHZ]	0.0	0.68(6)

a= not determinable directly from data set, calculated from planarity condition. b= difference A"-A' determined, value based on ground state value. c= constrained at the ground state value of NH_2OH.

TABLE VI

The α Constants $v_4 = 1$ and $v_5 = 1$ States
of NH_2OH and the Upper State
of the New Band of NHDOD

	$v_4=1(NH_2OH)$	$v_5=1(NH_2OH)$	$v_5=1(NHDOD)$
α^A [GHz]	-3.2	-0.39	-0.39
α^B [GHz]	0.12	0.12	0.12
α^C [GHz]	0.028	0.047	-0.047

It appears that further data on deuterated forms of hydroxylamine can certainly be obtained from the analysis of diode laser spectra. For example, the additional lines in Fig. 6b almost certainly arise from ND_2OD. However, the fact that it is difficult to control the composition of the sample will mean that considerable patience will be required if a complete investigation of the deuterated hydroxylamine system is to be carried out.

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