

# IR Vibration–Rotation Spectra of the Ammonia Molecule

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This paper addresses the investigation of the rotational structure of the  $\nu_2$  doublet IR absorption of gaseous ammonia, along with an analysis of the structure of ammonia relative to this spectrum. The spectrum is obtained using a commercial Fourier-transform spectrometer, and the analysis is accomplished in part using Maple (for the symbolic computation of the tensor of the moment of inertia).

## Experimental Procedure

The  $0.5\text{ cm}^{-1}$  nominal resolution (8192 point FFT) IR spectrum of ammonia may be easily obtained using a Fourier-transform IR Spectrometer, such as the MIDAC M series used in our teaching laboratory. A sample of ammonia-soaked filter paper, placed in the sample cavity of the spectrometer provides sufficient ammonia vapor to obtain a spectrum.

The interesting band, from this paper's point of view, is the "doublet" that occurs at about  $930$  and  $960\text{ cm}^{-1}$ . This absorption constitutes the fundamental absorption associated with the  $\nu_2$  normal mode of vibration corresponding to the motion of the nitrogen through the plane of the three protons (and vice versa). The spectrum we report here consists of about 82 separate "lines" in the region from  $800\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$ ; most appear to be complex, unresolved, overlapping absorptions (*vide infra*).

The doubling of this fundamental vibration is thought to be due to the barrier to umbrella inversion that the nitrogen encounters on its travels through the proton plane. If that barrier did not exist, this low frequency vibration would be normal in appearance. (See Fig. 1.)

The existence of the barrier results in a doubling of each vibrational-energy level, and a corresponding splitting in the observed transitions. We are therefore required to treat the symmetric and antisymmetric states of each vibrational level in parallel. The  $0(a) \rightarrow 1(s)$  transition is centered at about  $935\text{ cm}^{-1}$ , whereas the  $0(s) \rightarrow 1(a)$  transition is centered at about  $976\text{ cm}^{-1}$ .

## Analysis (1)

There are several aspects of the analysis that must be considered. We start here with the tensor of the moment of inertia that is associated with the rotation of the ammonia molecule, whether vibrating or not. We seek expressions for the nine elements of the tensor that involve the fundamental constants of the ammonia molecule, that is, the H–N–H angle and the distance between the nitrogen and any hydrogen atom. (We will treat the case in which all N–H distances are the same because we are treating that vibrational mode in which the molecule is flexing its nitrogen against the plane of the three protons.)

The classic formula for the tensor of the moment of inertia is given in all textbooks, although applications to other

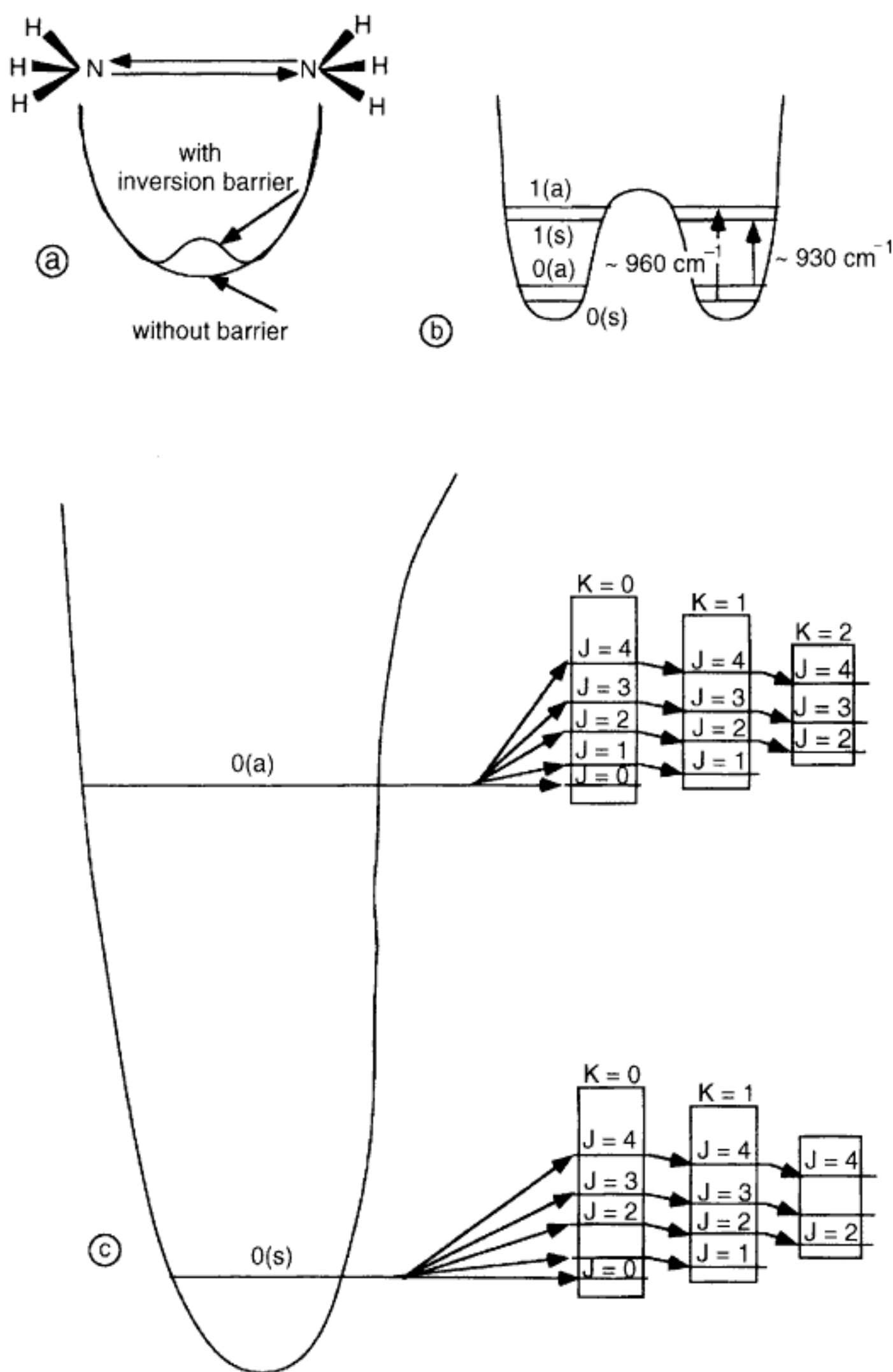


Figure 1. The energy levels for vibration and rotation in ammonia: For the  $\nu_2$  vibration, the rotational-energy levels are shown. (a) One sees the overall vibrational potential-energy well, with or without a barrier. (b) Schematically, the ground and first excited state of vibration, each state being doubled, (s) and (a). The  $\sim 960$  and  $\sim 930\text{ cm}^{-1}$  centered transitions are shown without fine structure. (c) The detailed energy levels of the ground states, (s) and (a).

than trivial examples usually are not given. We have used Maple<sup>1</sup> to obtain the following formulas.

We place the nitrogen atom on the negative  $z$ -axis; the three protons are in a plane parallel to the  $x$ - $y$  plane, but intercepting the  $z$ -axis on the positive side. The three protons are arranged  $120^\circ$  apart in their common plane, and we arbitrarily locate one of them with its  $y$ -coordinate set to zero.

The tensor of the moment-of-inertia computation requires that we place our coordinate system's origin at the center of mass (c.o.m.). In the case of ammonia, the c.o.m. lies on the  $z$ -axis, on a line joining the nitrogen to the center of the  $H_3$  triangle.

<sup>1</sup>Mathematica would do just as well, as would any symbolic mathematics program. The Maple source is available from the author, either by request using Internet address david@uconnvm.uconn.edu or by mail.

The moment-of-inertia tensor has components,

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2)$$

$$I_{yy} = \sum_i m_i (x_i^2 + z_i^2)$$

$$I_{zz} = \sum_i m_i (x_i^2 + y_i^2)$$

$$I_{xy} = \sum_i m_i x_i y_i$$

$$I_{xz} = \sum_i m_i x_i z_i$$

$$I_{yz} = \sum_i m_i y_i z_i$$

where the sum extends over all atoms in the system.

We use  $\alpha$  as the angle from the symmetry axis to the N-H bond and  $r$  as the N-H bond length so that we explicitly place the nitrogen below the  $x$ - $y$  plane; the three hydrogens at  $120^\circ$  in a plane parallel to the  $x$ - $y$  plane are at a height on the  $z$ -axis such that the c.o.m. of the entire molecule is at the origin. We obtain

$$\left\{ \begin{array}{lll} \frac{3/2 m_{\text{H}} r^2 (3m_{\text{H}} \sin^2 \alpha - m_{\text{N}} \sin^2 \alpha + 2m_{\text{N}})}{3m_{\text{H}} + m_{\text{N}}} & 0 & 0 \\ 0 & \frac{3/2 m_{\text{H}} r^2 (3m_{\text{H}} \sin^2 \alpha - m_{\text{N}} \sin^2 \alpha + 2m_{\text{N}})}{(3m_{\text{H}} + m_{\text{N}})} & 0 \\ 0 & 0 & 3m_{\text{H}} r^2 \sin^2 \alpha \end{array} \right.$$

Figure 2 shows the construction that leads to

$$\frac{4}{3}\sin^2 \frac{\theta}{2} = \sin^2 \alpha$$

so that, after substitution, we obtain

$$\left\{ \begin{array}{lll} \frac{m_{\text{H}} r^2 (2m_{\text{N}} + 3m_{\text{H}})}{3m_{\text{H}} + m_{\text{N}}} + \frac{m_{\text{H}} r^2 (m_{\text{N}} - 3m_{\text{H}}) \cos \theta}{3m_{\text{H}} + m_{\text{N}}} & 0 & 0 \\ 0 & \frac{m_{\text{H}} r^2 (2m_{\text{N}} + 3m_{\text{H}})}{3m_{\text{H}} + m_{\text{N}}} + \frac{m_{\text{H}} r^2 (m_{\text{N}} - 3m_{\text{H}}) \cos \theta}{3m_{\text{H}} + m_{\text{N}}} & 0 \\ 0 & 0 & 2m_{\text{H}} r^2 (1 - \cos \theta) \end{array} \right.$$

and we can further manipulate the  $xx$  and  $yy$  terms to the form

$$\frac{m_H r^2 (2m_N + 3m_H)}{m} + \frac{m_H r^2 (m_N - 3m_H) \cos \theta}{m}$$

where

$$m = 3m_{\text{H}} + m_{\text{N}}$$

so that

$$I_{xx} = I_{yy} = \frac{m_H r^2 \left( (m_N + m) + (2m_N - 3m_H - m_N) \cos \theta \right)}{m}$$

which becomes

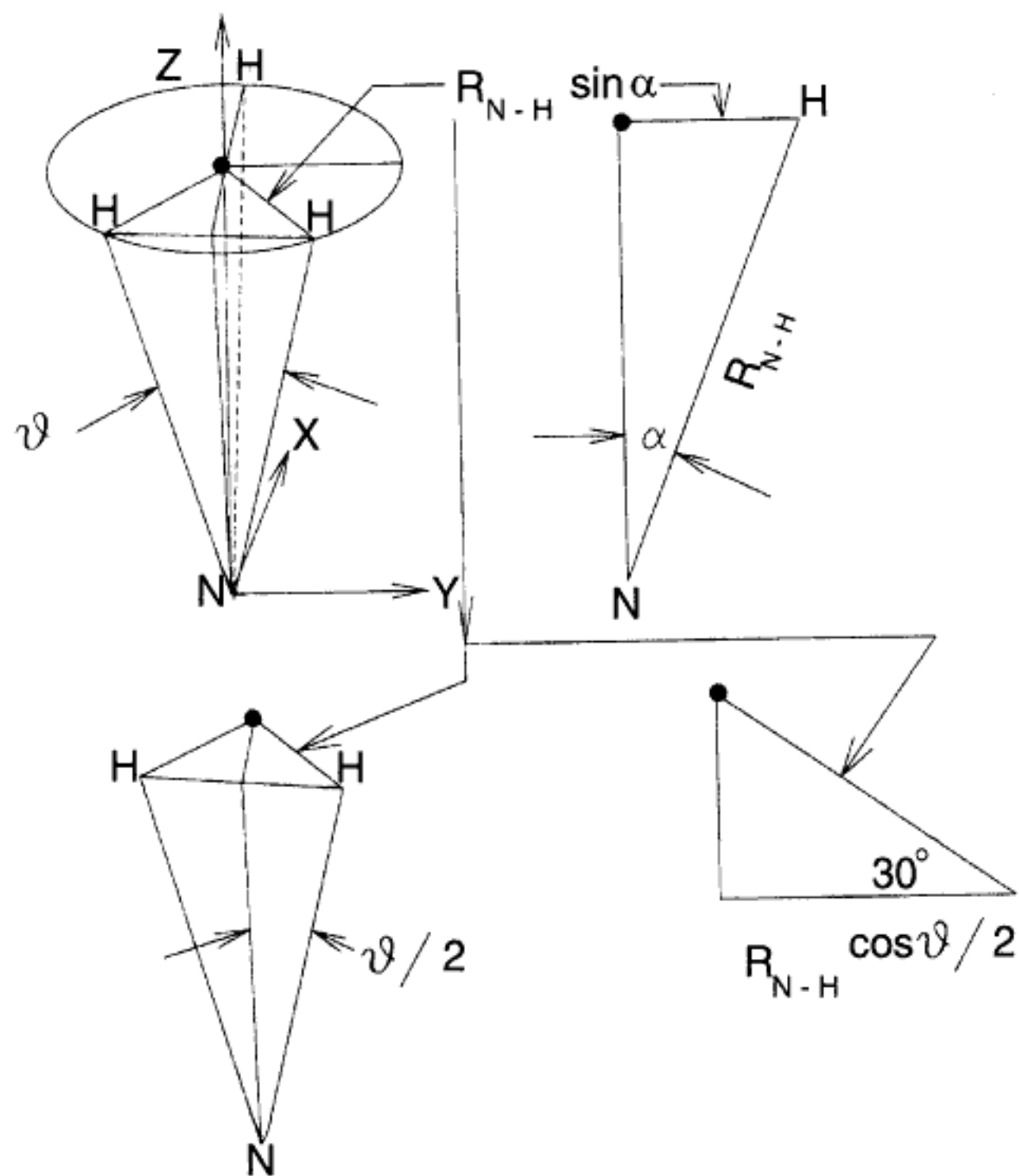


Figure 2. The geometry of the ammonia molecule: The nitrogen atom lies below the  $x$ - $y$  plane. The intersection of the H-plane with the  $z$ -axis is marked with a fiducial filled-in circle. Also shown are the relations required to convert from the  $\alpha$  to the  $\theta$ .

$$\frac{m_{\text{H}} r^2 \left( (m_{\text{N}} + m) + (2m_{\text{N}} - m) \cos \theta \right)}{m}$$

which is

$$\left. \begin{array}{l} 0 \\ \frac{(m_N - 3m_H)\cos\theta}{3m_H + m_N} \\ 2m_H r^2(1 - \cos\theta) \end{array} \right\}$$

$$\frac{m_{\text{H}}mr^2(1 - \cos \theta)}{m} + \frac{m_{\text{H}}r^2(m_{\text{N}} + 2m_{\text{N}}\cos \theta)}{m}$$

which finally is

$$I_{xx} = I_{yy} = m_H r^2 (1 - \cos \theta) + \frac{m_H m_N r^2 (1 + 2 \cos \theta)}{m}$$

while

$$I_{zz} = 2m_H r^2 (1 - \cos \theta)$$

Atkins (1a) reports the same values.

We can verify that these equations give the "right" numerical value by appropriately substituting, that is, where

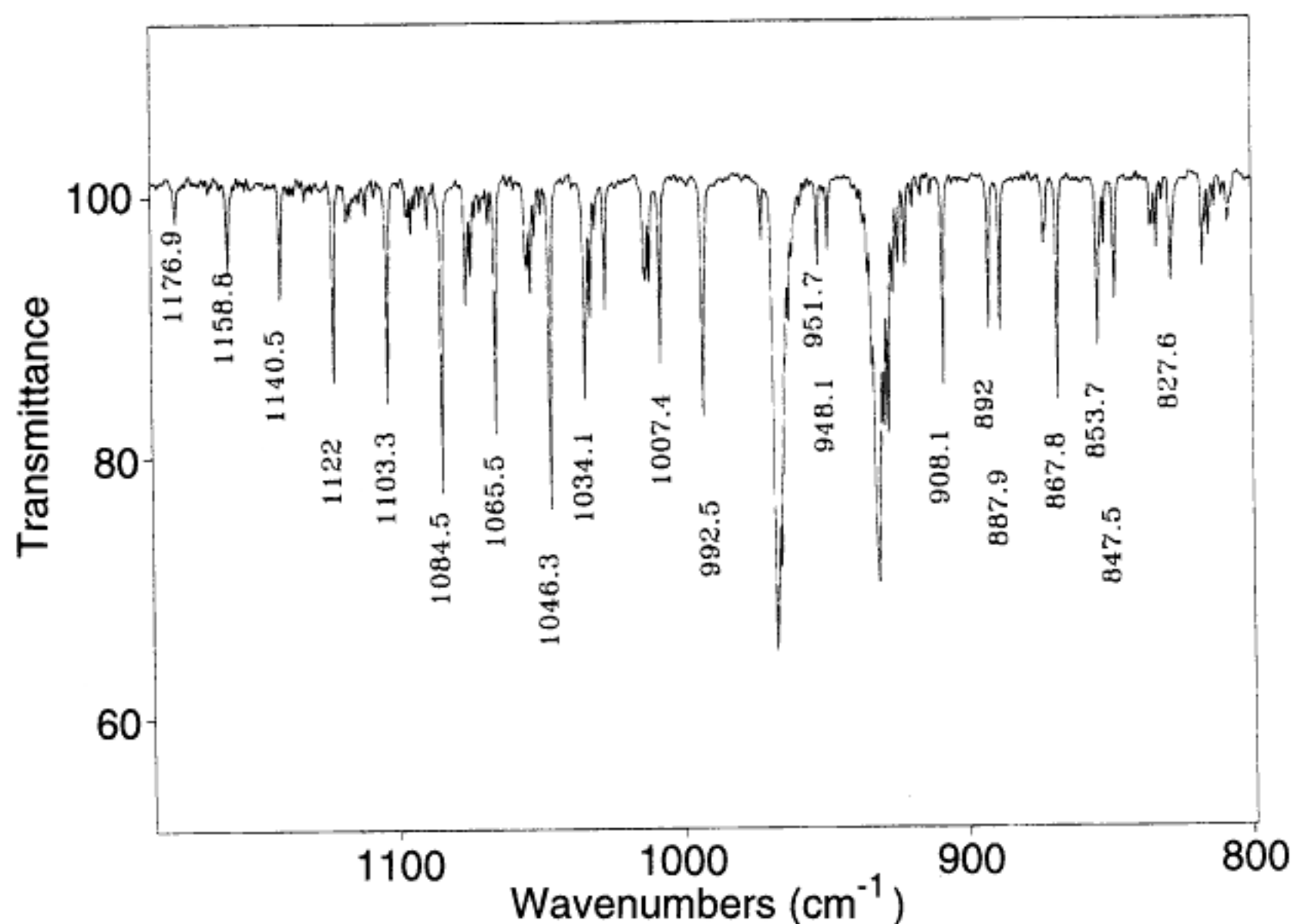


Figure 3. The overall rotation–vibration spectrum for the inversion normal mode: For the  $\nu_2$  vibration, the spectrum from  $\approx 1200\text{ cm}^{-1}$  to  $\approx 800\text{ cm}^{-1}$ . Several wavelengths are shown directly on the trace belonging to either the  $0(a) \rightarrow 1(s)$  or the  $0(s) \rightarrow 1(a)$  transition group.

$\alpha \approx 67^\circ$  and  $r_{\text{N-H}} = 1.012\text{ \AA}$ . The matrix turns out to be a priori diagonal in this coordinate system, with values

$$I_{yy} = I_{xx} = 0.2902547181 \times 10^{-39} \text{ gm cm}^2$$

$$I_{zz} = 0.4322366435 \times 10^{-39} \text{ gm cm}^2$$

where the extraordinary number of reported figures is Maple's way of reminding us that it can compute to any accuracy desired, even if that "accuracy" is more than the inputted numbers provided! Atkins (1a, p 440) gives values

$$I_{yy} = I_{xx} = 0.2805 \times 10^{-48} \text{ kg m}^2$$

$$I_{zz} = 0.4412 \times 10^{-48} \text{ kg m}^2$$

where he has used  $m_{\text{H}} = 1.0078$  and  $m_{\text{N}} = 14.003$  with  $r_{\text{N-H}} = 1.012\text{ \AA}$ , and  $\theta = 106.7^\circ$ .

The moments of inertia can be used to predict the expected vibrational–rotational spectrum, or the spectrum can be used to obtain the values of  $\alpha$  (or  $\theta$ ) and  $r_{\text{N-H}}$ . We get the following values.

$$B = 10.00104776 \text{ cm}^{-1}$$

and

$$C = 6.449122069 \text{ cm}^{-1}$$

Atkins (1a) uses  $A$  and  $B$  as the rotational constants, whereas for an oblate top molecule such as this,

$$I_A = I_B < I_C$$

as properly noted by Vemulapalli (1b).

Because, to a beginning approximation, the rotational-energy levels are given by the formula

$$\frac{E_{J,K}}{hc} = BJ(J+1) + (C-B)K^2$$

in  $\text{cm}^{-1}$  we have for this geometry

$$\frac{E_{J,K}}{hc} = 10.0J(J+1) + (6.4 - 10.0)K^2$$

for the assumed geometry.

Where our example assumes molecular constants and obtains rotational constants, the experimental situation is the reverse. If we could infer the values of  $B$  and  $C$  from the observed energy levels, then we could obtain some information about the geometry of the ammonia molecule (at worst by trial and error through Maple computations).

## Analysis (2)

In Figure 1 we see a schematic of the relationship between the potential energy surface for the  $\nu_2$  vibration, the vibrational-energy levels, and the rotational-energy levels that are needed for an understanding of the spectrum under consideration.

The actual IR spectrum obtained in our laboratory is shown in Figure 3. The underlying rotational sublevels of the relevant vibrational-energy levels is shown in Figure 4.

The assignment of rotational frequencies for the  $0(a) \rightarrow 1(s)$  vibrational band, for the  $K = 0$  states, is given in Table 1, along with the theoretical values computed from the data in Table 7 (2), whereas those for the  $0(s) \rightarrow 1(a)$  band, again for  $K = 0$  states, is given in Table 2. It will be seen that these values, both experimental and calculated, are in reasonably good accord; also, they are in substantial agreement

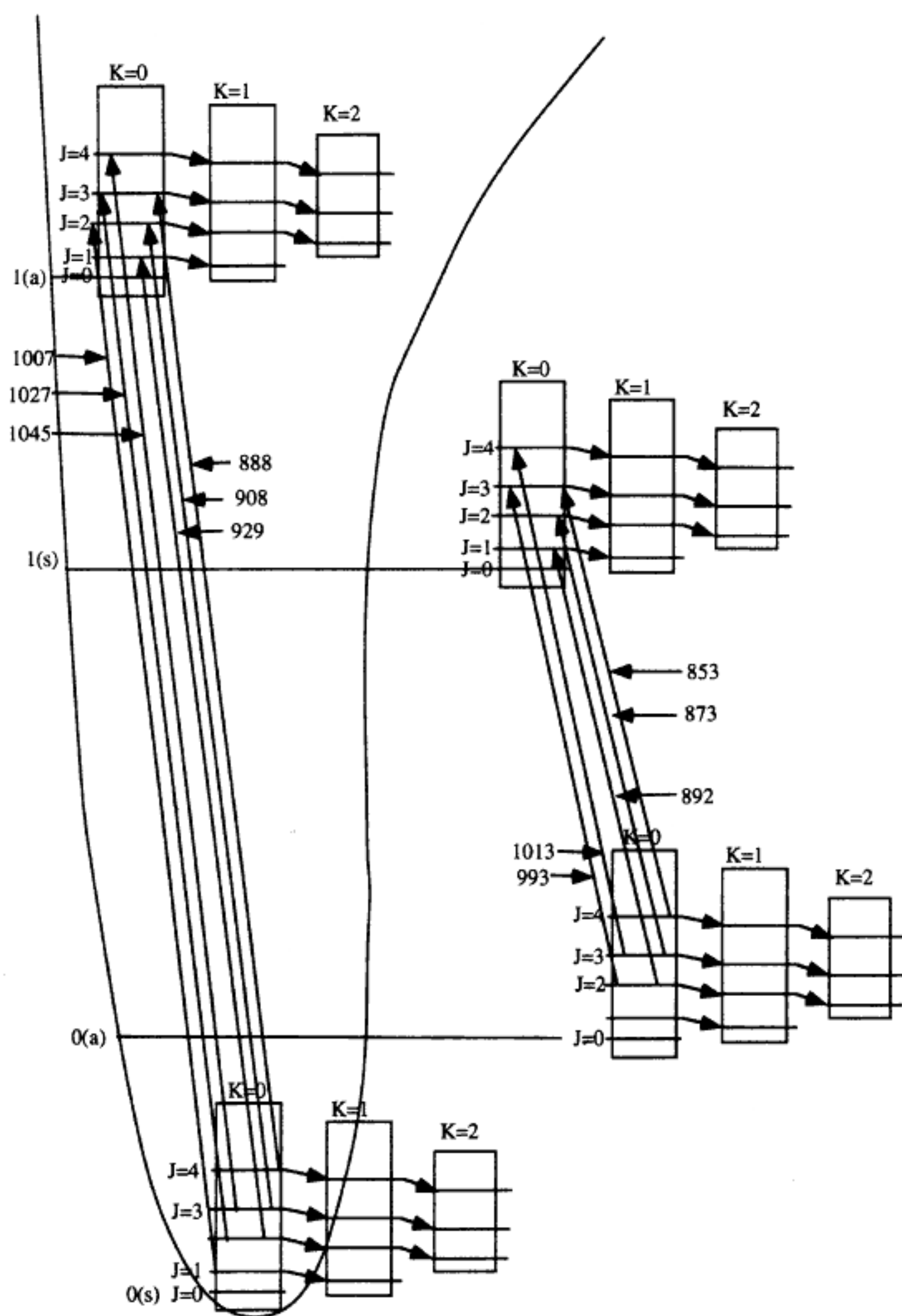


Figure 4. Schematic relation of energy levels to observed transitions: For the  $\nu_2$  vibration, the energy levels involved in some of the  $0(a) \rightarrow 1(s)$  transitions (right side) and some of the  $0(s) \rightarrow 1(a)$  transitions (left side).



**Table 1. Assignment of  $K = 0$  Spectrum,  $0(a) \rightarrow 1(s)$** 

Literature Value (computed)	Experimental Values	$J \rightarrow J'$		$\kappa$		
798.4817	798.0795	7	6	7	Experimental	
816.651	816.4573	6	5	6	Regression Output:	
835.0932	834.716	5	4	5	Constant	934.5772
853.8179	853.652	4	3	4	Std. Err. of Y Est.	2.021107
872.8414	872.4502	3	2	3	R Squared	0.99972
892.1567	892.0124	2	1	2	No. of Observations	13
992.6988	992.529	2	3	-3	Degrees of Freedom	11
1013.418	1012.973	3	4	-4	X Coefficient	-19.9998
1034.245	1034.06	4	5	-5	Std. Err. of Coef.	0.100842
1055.134	1054.273	5	6	-6	Literature	
1076.033	1075.827	6	7	-7	Regression Output:	
1096.889	1095.018	7	8	-8	Constant	935.2367
1117.648	1117.453	8	9	-9	Std. Err. of Y Est.	2.114762
1138.257	1140.5	9	10	-10	R Squared	0.999776
1158.667		10	11	-11	No. of Observations	17
1178.831		11	12	-12	Degrees of Freedom	15
1198.708		12	13	-13	X Coefficient	-20.1729
					Std. Err. of Coef.	0.078051

The  $0(a) \rightarrow 1(s)$  is often referred to as the  $0^+ \rightarrow 1^-$  transition. The theoretical values are calculated from the energy levels in Table 7.

with those of Nakanaga et al. (3). From these two, by linear regression against a running index,  $\kappa$ , we obtain  $B$  values of  $19.9998/2$  (i.e.,  $9.9999 \text{ cm}^{-1}$  and  $19.4808/2$ , or  $9.2404 \text{ cm}^{-1}$ ) for the two sets of transitions studied: the rotational-energy levels of the  $\nu_2$  vibrational state in ammonia.

From the Maple analysis, we obtain the equation

$$9.9999 = \frac{0.2797731183 \times 10^{-38}}{(0.3027609848 \times 10^{-23} + 0.1074313172 \times 10^{-23} \cos \theta) r_{N-H}^2}$$

(with  $r$  expressed in centimeters) for the relation between the N-H distance and the H-N-H angle. This equation predicts values in close agreement with the expected values.

Once these lines are "removed" from consideration, it becomes apparent that there are many lines in the spectrum yet unaccounted for, which is a cause of some concern. Herzberg (4) shows a drawing of the spectrum taken from Sheng et al. (5) showing explicit designations both of the R and P branches of each of the two subfrequencies ( $960$  and  $930 \text{ cm}^{-1}$ ), but two Q-branches as well, one for each subfrequency. As can be seen in our own version of this spectrum, the Q-branch of the  $930 \text{ cm}^{-1}$  transition is shaded in both P and R directions, whereas the  $960 \text{ cm}^{-1}$  transition has the more normal P-direction shading. In Tables 3-6 we attempt an assignment of these Q-branches. The actual (enlarged) spectrum of the two bands in question appears in Figure 5.

The  $960 \text{ cm}^{-1}$  band shows a Q-branch that appears to be transitions from the  $J, K = J$  (rather than  $K = 0$ ) to the same  $J$  (and  $K$ ) value in the higher state. Several transitions are not resolved in our spectrum, so the assignment is based on a little guesswork. For the  $930 \text{ cm}^{-1}$  band, there are two distinct shadings, one involving the J-to-J transitions with  $K = 0$ , and the other involving the J-to-J transitions with  $K = J$ .

## Discussion

The ongoing rush of technical improvements makes experiments that once were suitable solely for specialists ac-

cessible to undergraduates. In the case treated in this paper, two ongoing advances make it possible to obtain and analyze a part of the ammonia spectrum, and obtain results of typically remarkable spectroscopic accuracy. First, the availability of Maple (and Mathematica, Macsyma, etc.) means that formulas for the tensor of the moment of inertia can now be constructed simply and easily without undue trauma. The tensor so obtained can then be diagonalized (in symbolic form) and evaluated.

Second, the ability to take the medium-resolution IR spectrum of a molecule as complex as ammonia, and obtain sufficient numbers of ab-

**Table 2. Assignment of  $K = 0$  Spectrum,  $0(s) \rightarrow 1(a)$** 

Literature Value (Computed)	Experimental Values	$J \rightarrow J'$		$\kappa$		
827.8777	827.6035	7	6	7	Experimental	
847.9147	847.5351	6	5	6	Regression Output	
868.0016	867.7689	5	4	5	Constant:	966.2207
888.1067	887.9022	4	3	4	Std. Err. of Y Est.	1.922892
908.1992	908.0801	3	2	3	R Squared	0.999754
928.2499	928.8162	2	1	2	No. of Observations	16
1007.547	1007.446	1	2	-2	Degrees of Freedom	14
1027.052	1026.936	2	3	-3	X Coefficient(s)	-19.4808
1046.405	1046.303	3	4	-4	Std. Err. of Coef.	0.081714
1065.599	1065.451	4	5	-5	Literature	
1084.629	1084.486	5	6	-6	Regression Output:	
1103.492	1103.327	6	7	-7	Constant	966.2209
1122.185	1122.03	7	8	-8	Std. Err. of Y Est.	2.404001
1140.708	1140.5	8	9	-9	R Squared	0.999664
1159.056	1158.838	9	10	-10	No. of Observations	18
1177.227	1176.922	10	11	-11	Degrees of Freedom	16
1195.217		11	12	-12	X Coefficient(s)	-19.3414
1213.019		12	13	-13	Std. Err. of Coef.	0.088583

Similarly, the  $0(s) \rightarrow 1(a)$  is often designated  $0^- \rightarrow 1^+$ .

**Table 3. Fine Structure of the  $930 \text{ cm}^{-1}$  Transition**

Literature Value	Observed	$J$	Comments
931.6405	931.7	0	
931.8965		1	not observed
932.4013	932.8197	2	
933.2411		3	not observed

$\Delta K = 0, \Delta J = 0, K = 0$  throughout.

**Table 4. The Q-Branch for the  $0(a) \rightarrow 1(s)$  Transition**

Literature Value	Observed	$J$
930.7571	930.9	0
929.8981	929.9	4
928.7545	928.8	5
927.3230	927.3	6
925.5996	925.6	7
923.5797	923.6	8
921.2552	921.2	9
918.6207	918.6	10

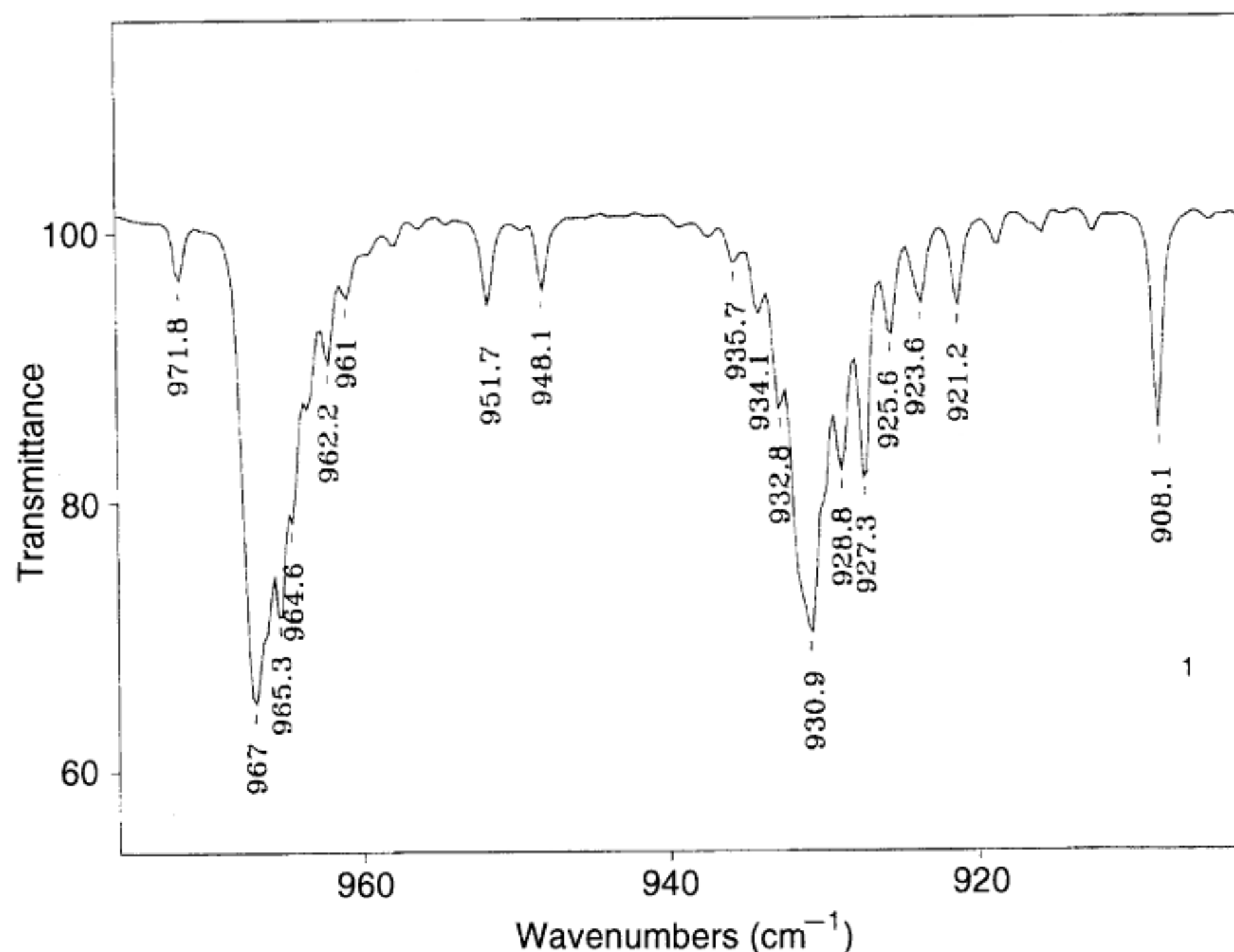


Figure 5. The  $\approx 960\text{ cm}^{-1}$  and  $\approx 930\text{ cm}^{-1}$  bands expanded: The Q branch structure of the two central bands are shown here expanded.

**Table 5. Part of the Fine Structure of the  $0(s) \rightarrow 1(a)$  Transition**

Literature Value	Observed	$J$	Comments
968.122		0	not observed
968.0093		1	
967.7877		2	not observed
967.464		3	
967.0482		4	not observed
966.5526		5	
965.9911		6	not observed
965.3783		7	
964.7288			
964.0563			

$\Delta K = 0$ ,  $\Delta J = 0$ ,  $K = 0$  throughout.

**Table 6. The Q-branch for the  $0(s) \rightarrow 1(a)$  Transition**

Literature Value	Observed	$J$
967.9978		1
967.74		2
937.3464	967.0104	3
966.8147		4
966.1511		5
965.3539	965.349	6

$\Delta K = 0$ ,  $\Delta J = 0$ ,  $K = J$  throughout.

**Table 7. Literature Values. Spin-Forbidden Energy Levels Indicated in Brackets**

$J$	$K$	Ground State		Excited State	
		s	a	s	a
0	0	(0)	0.793403	(932.4339)	968.122
1	0	19.88989	(20.67325)	952.5697	(987.8992)
1	1	16.17299	16.96335	948.5912	984.1708
2	0	(59.64933)	60.41301	(992.8143)	1027.437
2	1	55.93872	56.70921	988.8454	1023.714
2	2	44.79598	45.58728	976.9206	1012.534
3	0	119.2378	(119.973)	1053.112	(1086.702)
3	1	115.5366	116.2783	1049.159	1082.986
3	2	104.4221	105.1837	1037.278	1071.829
3	3	85.86159	86.65781	1017.415	1053.208
4	0	(198.5951)	199.2939	(1133.391)	1165.643
4	1	194.9063	195.6113	1129.454	1161.937
4	2	183.8291	184.553	1117.629	1150.81
4	3	165.3311	166.0879	1097.861	1132.236
4	4	139.358	140.1632	1070.061	1106.173
5	0	297.6418	(298.2977)	1233.539	(1264.194)
5	1	293.9683	294.63	1229.624	1260.501
5	2	282.9371	283.6167	1217.869	1249.411
5	3	264.5166	265.2266	1198.219	1230.897
5	4	238.6526	239.4082	1170.586	1204.922
5	5	205.2691	206.0874	1134.842	1171.42
6	0	(416.2796)	416.8877	(1353.432)	1382.271
6	1	412.6243	413.2378	1349.543	1378.592
6	2	401.6478	402.2777	1337.869	1367.547
6	3	383.3184	383.9775	1318.357	1349.11
6	4	357.5842	358.2845	1290.921	323.236
6	5	324.3689	325.1272	1255.434	1289.868
6	6	283.5743	284.4101	1211.733	1248.928

sorption lines to allow assignment of the rotational constant is amazing.

The understanding derived from analyzing a complex rotation-vibration spectrum should thoroughly cement the principles involved into the matrix of understanding that chemists need in facing the modern, highly instrumented (blackbox) world.

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