JOURNAL OF MOLECULAR SPECTROSCOPY 127, 415–424 (1988)

Fourier Transform Infrared Spectrum of the ν_2 Band of the NH_2 Radical

JAMES B. BURKHOLDER AND CARLETON J. HOWARD

NOAA Aeronomy Laboratory, R/E/AL2, 325 Broadway, Boulder, Colorado 80303, and Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, Colorado 80302

AND

A. R. W. MCKELLAR

Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

The ν_2 fundamental band of NH_2 has been observed at high resolution (0.0045 cm^{-1}) using a Fourier transform infrared spectrometer and a fast-flow multiple-traversal absorption cell. A total of 336 lines were measured with an accuracy of about 0.0004 cm^{-1} and assigned to NH_2 transitions with values of the rotational quantum numbers N and K_a up to 10 and 5, respectively. These data greatly improve the precision of our knowledge of the ν_2 line positions and the $(v_1v_2v_3) = (010)$ vibrational state molecular parameters.

I. INTRODUCTION

Spectra of the NH_2 radical have been extensively studied over a wide range of frequencies using many different experimental techniques. For the ground and excited vibrational levels of the $\tilde{X}^2B_1$ ground electronic state, much information has been obtained from studies of the $\tilde{A}^2A_1$–$\tilde{X}^2B_1$ electronic spectrum in emission, in absorption, and by laser-induced fluorescence (*1–8*). Direct observations of vibrational transitions in the X state have included matrix isolation infrared absorption (*9*), infrared laser magnetic resonance (LMR) of ν_2 (*10, 11*), tunable diode laser absorption of ν_2 (*5, 12*), tunable difference laser absorption of ν_1 and ν_3 (*13*), and coherent antistokes Raman (CARS) detection of ν_1 (*14*).

In the present paper, we report a study of the ν_2 fundamental band of NH_2 in its ground electronic state by the technique of high-resolution Fourier transform absorption spectroscopy. Although this band has already been quite well characterized (*5*), it turns out that our measurements are more precise than those from electronic spectroscopy (*3, 5*) and considerably more complete than those from LMR spectroscopy (*10, 11*). As a result, the ν_2 line positions and associated molecular parameters are determined here with significantly higher accuracy than was previously available (*5*). This result is valuable both because of the central role played by NH_2 in free radical studies and because high accuracy may be essential for future applications in which the ν_2 band is used to detect and monitor the presence of NH_2 (for example, in laboratory kinetics experiments or infrared astronomy of interstellar clouds).

0022-2852/88 $3.00

II. EXPERIMENTAL DETAILS

The apparatus has been previously used to study infrared spectra of a number of free radicals (*15–17*) and is described in detail by Burkholder *et al.* (*18*). A Bomem Fourier transform spectrometer (Model DA3.002) was used at a resolution of 0.0045 cm^{-1} (apodized) together with a fast-flow multiple-traversal absorption cell. The source was an incandescent carbon rod, the beam splitter was KCl, and the detector was liquid helium-cooled Cu:Ge. The spectrum was recorded in two sections: 1200 to 1570 cm^{-1} and 1550 to 1850 cm^{-1}. Absolute wavenumber calibration was made by means of accurately known lines of the N_2O molecule, using the ν_1 band (*19*) for the lower frequency section and $\nu_2 + \nu_3$ (*20*) for the higher frequency section.

NH_2 was formed from the reaction of atomic fluorine with excess ammonia

$$F + NH_3 \rightarrow NH_2 + HF \quad (1)$$

for which $k_1 = 8 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} at 298 K (*21*). The primary loss processes for the NH_2 radical are by the reactions

$$NH_2 + NH_2 \rightarrow \text{products} \quad (2)$$

for which $k_2 = 1.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} (*22*) and

$$NH_2 + \text{wall} \rightarrow \text{products} \quad (3)$$

for which $\gamma < 3 \times 10^{-3}$ (*21*). Fluorine atoms were generated in three microwave discharges of a 10% F_2 in He mixture. The discharge tubes contained alumina tubing inserts to reduce the Pyrex deterioration over prolonged exposure to F atoms. Ammonia was added ($\approx 10^{13}$ molecule cm^{-3}) to the absorption cell behind the nesting mirror, and reaction (1) occurred directly in the optical path. The maximum NH_2 signals were obtained with the minimum achievable residence time in the absorption cell, $\approx$0.075 s. Spectra were recorded at a total cell pressure of 0.15 Torr.

III. RESULTS

NH_2 is a light asymmetric rotor molecule whose structure and infrared spectrum resemble those of water vapor. Unlike H_2O, however, NH_2 has a doublet ground electronic state with a net unpaired electron spin of $S = \frac{1}{2}$. Each rotational level, denoted by the asymmetric rotor quantum numbers $N_{K_aK_c}$, is split into two levels with $J = N + 1/2$ (F_1 sublevel) and $J = N - 1/2$ (F_2 sublevel) by spin–rotation interaction. Rotational and vibration–rotation transitions are dominated by the selection rules $F_1 \leftrightarrow F_1$ and $F_2 \leftrightarrow F_2$, with the result that each transition of the ν_2 band is split into an F_1 and an F_2 component. *ortho*-NH_2 levels with (K_a, K_c) = (even, even) or (odd, odd) have a nuclear spin statistical weight of 3 with respect to *para*-NH_2 levels with (K_a, K_c) = (even, odd) or (odd, even). Hyperfine splittings, which were not resolved in the present work, occur in NH_2 due to interactions involving the ^{14}N nuclear spin ($I_N = 1$), as well as the resultant proton spin ($I_H = 1$) in the case of *ortho* levels.

A small portion of the observed spectrum around 1445 cm^{-1} is shown as an example in Fig. 1. In this region, the only features observed in addition to those assigned to NH_2 are some relatively weak NH_3 lines. At higher frequencies, above 1500 cm^{-1}, there were many stronger lines observed in the spectrum due to the ν_4 and $2\nu_2$ bands

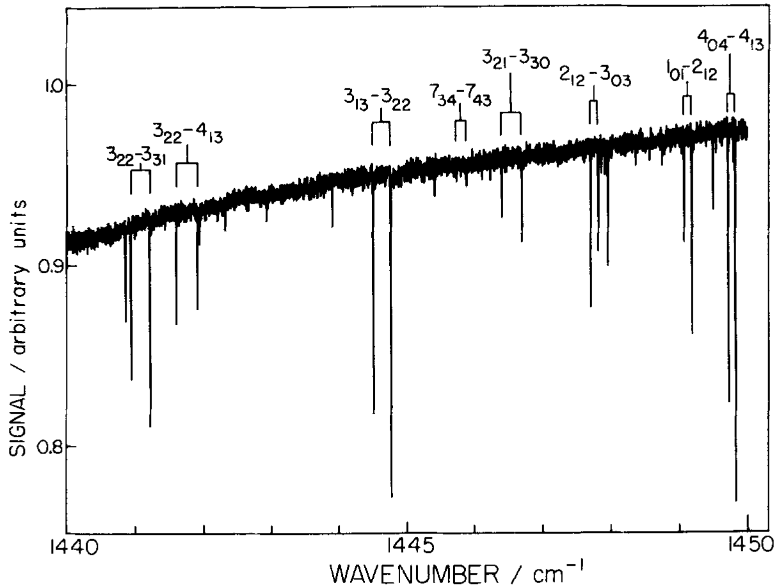

FIG. 1. A small portion of the spectrum of the ν_2 band of NH_2 observed in absorption with a resolution of 0.0045 cm^{-1}. Indicated are eight spin doublets assigned to NH_2 (see Table I). The unassigned lines in this region are due to NH_3.

of NH_3. The measured wavenumbers and assignments of 336 transitions of the ν_2 band of NH_2 are listed in Table I, which includes values of N up to 10 and of K_a up to 5. Even though the rotational structure of the band is highly irregular on casual inspection, the assignments were made quite easily. First, some 280 lines were assigned on the basis of calculated positions from the parameters of Birss *et al.* (5), and then the parameters were refined (see below) and the remaining lines assigned. Since both NH_2 and NH_3 have relatively uncongested spectra, there were only a few cases where NH_2 lines had to be omitted because of blending with NH_3 lines and only two cases of NH_2 overlapping with itself (see Table I). Transitions of the type $F_1 \leftrightarrow F_2$ have significant intensity only for low values of N, and in the present case they were observed only for the $1_{11} \leftrightarrow 0_{00}$ and $1_{10} \leftrightarrow 1_{01}$ transitions (see Table I).

Although the Bomem spectrometer is capable of line measurement accuracies of 0.0002 cm^{-1} or better in the present spectral region, the NH_2 data are limited to an accuracy of perhaps ± 0.0004 cm^{-1}. There are two main reasons for this. First, the signal to noise ratio of the spectra is rather modest, ranging from about 50 for the strongest lines to about 2 for the weakest. Second, there is some evidence that NH_2 hyperfine structure is on the verge of being resolved for some of the transitions, causing slightly asymmetric lineshapes in these cases. The wavenumber found by the line position measuring routine may then not correspond exactly to the true center of gravity of the line. We endeavored to minimize this effect at the expense of a slight loss in resolution by using the apodized, rather than unapodized, spectrum in our analysis.

TABLE I

Observed Wavenumbers (cm⁻¹) of Assigned Transitions in the ν_2 Band of NH_2[a]

F	N	K_a	K_c	← F	N	K_a	K_c	OBSERVED	O-C
2	6	4	2	2	7	5	3	1270.9474	-4
1	6	4	2	1	7	5	3	1270.9861	0
2	6	3	4	2	7	4	3	1271.6602	-1
1	6	3	4	1	7	4	3	1271.7365	2
2	6	3	3	2	7	4	4	1288.0731	-2
1	6	3	3	1	7	4	4	1288.1878	4
1	5	2	4	1	6	3	3	1290.7855	-3
2	5	4	1	2	6	5	2	1291.7395	0
1	5	4	1	1	6	5	2	1291.7520	4
2	5	3	3	2	6	4	2	1297.6694	-1
1	5	3	3	1	6	4	2	1297.7533	0
1	5	3	2	1	6	4	3	1303.7691	3
1	4	4	1	1	5	5	0	1313.1425	6
1	4	4	0	1	5	5	1	1313.1731[b]	8
2	4	4	1	2	5	5	0	1313.1731[b]	-21
2	4	4	0	2	5	5	1	1313.2048	-6
2	4	3	2	2	5	4	1	1321.0139	-1
1	4	3	2	1	5	4	1	1321.0906	-5
2	4	3	1	2	5	4	2	1322.5805	0
1	4	3	1	1	5	4	2	1322.6658	0
2	6	2	4	2	7	3	5	1324.6749	0
1	6	2	4	1	7	3	5	1324.7735	-1
2	4	2	3	2	5	3	2	1324.7957	12
1	4	2	3	1	5	3	2	1324.9244	-2
2	5	2	3	2	6	3	4	1333.3994	2
1	8	1	7	1	9	2	8	1333.4727	4
2	8	1	7	2	9	2	8	1333.5137	11
2	10	0	10	2	10	1	9	1334.8201	6
1	10	0	10	1	10	1	9	1335.0042	-2
1	8	2	7	1	9	1	8	1336.6902	1
2	8	2	7	2	9	1	8	1336.7568	-11
1	8	0	8	1	9	1	9	1339.6624	2
2	8	0	8	2	9	1	9	1339.6843	0
1	8	1	8	1	9	0	9	1339.7743	0
2	8	1	8	2	9	0	9	1339.7969	-2
2	3	3	1	2	4	4	0	1343.1861	-1
1	3	3	1	1	4	4	0	1343.2306	0
2	3	3	0	2	4	4	1	1343.4122	0
1	3	3	0	1	4	4	1	1343.4577	0
2	4	2	2	2	5	3	3	1345.0189	1
1	4	2	2	1	5	3	3	1345.1637	0
2	3	1	3	2	4	2	2	1346.1144	-1
1	3	1	3	1	4	2	2	1346.3247	-2
1	7	1	6	1	8	2	7	1347.0862	3
2	7	1	6	2	8	2	7	1347.1073	1
2	9	1	9	2	9	2	8	1352.8331	-2
1	9	1	9	1	9	2	8	1353.0199	2
2	3	2	2	2	4	3	1	1353.0555	1
1	3	2	2	1	4	3	1	1353.1966	-3
1	7	2	6	1	8	1	7	1353.6889	-5
2	7	2	6	2	8	1	7	1353.7660	-6
1	7	0	7	1	8	1	8	1356.9220	2
2	7	0	7	2	8	1	8	1356.9420	0
1	7	1	7	1	8	0	8	1357.1929	0
2	7	1	7	2	8	0	8	1357.2153	0
2	6	1	5	2	7	2	6	1359.2306	7
1	6	1	5	1	7	2	6	1359.2363	-5
2	3	2	1	2	4	3	2	1360.1995	2
1	3	2	1	1	4	3	2	1360.3519	-1
1	7	3	5	1	8	2	6	1365.4744	1
2	7	3	5	2	8	2	6	1365.6877	-2
2	5	1	4	2	6	2	5	1369.9193	0
1	5	1	4	1	6	2	5	1369.9615	4
2	8	1	8	2	8	2	7	1370.8076	-1
1	8	1	8	1	8	2	7	1370.9932	0
1	6	2	5	1	7	1	6	1371.9883	-5
2	6	2	5	2	7	1	6	1372.0862	-4
2	8	0	8	2	8	1	7	1372.2593	0
1	8	0	8	1	8	1	7	1372.4332	0
1	6	0	6	1	7	1	7	1373.8515	1
2	6	0	6	2	7	1	7	1373.8683	0
1	6	1	6	1	7	0	7	1374.5032	0
2	6	1	6	2	7	0	7	1374.5264	1
2	2	2	1	2	3	3	0	1377.3961	3
1	2	2	1	1	3	3	0	1377.5247	-4
2	2	2	0	2	3	3	1	1378.8418	5
1	2	2	0	1	3	3	1	1378.9635	-3
2	4	1	3	2	5	2	4	1380.1200	-1
1	4	1	3	1	5	2	4	1380.2011	0
2	2	1	2	2	3	2	1	1383.6088	0
1	2	1	2	1	3	2	1	1383.8300	-3
2	7	1	7	2	7	2	6	1388.2629	0
1	7	1	7	1	7	2	6	1388.4487	0
2	9	2	8	2	9	3	7	1388.7448	-1
1	9	2	8	1	9	3	7	1388.8555	-6
1	5	0	5	1	6	1	6	1390.3009	1
2	5	0	5	2	6	1	6	1390.3110	-1
2	3	1	2	2	4	2	3	1391.3051	-1
2	7	0	7	2	7	1	6	1391.3567	1
1	3	1	2	1	4	2	3	1391.4253	1
1	7	0	7	1	7	1	6	1391.5186	0
1	5	1	5	1	6	0	6	1391.8336	1
2	5	1	5	2	6	0	6	1391.8602	2
1	5	2	4	1	6	1	5	1392.4750	0
2	5	2	4	2	6	1	5	1392.6117	0
2	8	2	7	2	8	3	6	1402.6498	8
1	8	2	7	1	8	3	6	1402.7680	7
2	2	1	1	2	3	2	2	1404.6310	-2
1	2	1	1	1	3	2	2	1404.7934	0
2	6	1	6	2	6	2	5	1404.8705	2
1	6	1	6	1	6	2	5	1405.0594	0
2	4	0	4	2	5	1	5	1406.0124[b]	13
1	4	0	4	1	5	1	5	1406.0124[b]	-9
1	4	1	4	1	5	0	5	1409.4588	2
2	4	1	4	2	5	0	5	1409.4947	4
2	6	0	6	2	6	1	5	1410.9865	-2
1	6	0	6	1	6	1	5	1411.1314	2
2	9	3	7	2	9	4	6	1412.7656	1
1	9	3	7	1	9	4	6	1412.8532	-1
2	1	1	1	2	2	2	0	1414.3021	5
1	1	1	1	1	2	2	0	1414.5271	-2
2	7	2	6	2	7	3	5	1414.9131	4
1	7	2	6	1	7	3	5	1415.0431	1
2	8	1	7	2	8	2	6	1415.4195	4
1	8	1	7	1	8	2	6	1415.4716	6
1	4	2	3	1	5	1	4	1415.7969	12
2	4	2	3	2	5	1	4	1415.9972	8
2	5	1	5	2	5	2	4	1420.1519	0
1	5	1	5	1	5	2	4	1420.3502	-1
2	1	1	0	2	2	2	1	1420.6594	4
2	3	0	3	2	4	1	4	1420.7117	-1
1	3	0	3	1	4	1	4	1420.7400	1
1	1	1	0	1	2	2	1	1420.8494	-3
1	5	4	2	1	5	5	1	1421.8365	-3
1	5	4	1	1	5	5	0	1422.0553	4
2	6	4	2	2	6	5	1	1422.9793	2

[a] The columns headed F denote the spin state, with F = 1 for F_1 levels (J = N + 1/2) and F = 2 for F_2 levels (J = N - 1/2). The columns headed O-C denote observed minus calculated wavenumbers in units of 0.0001 cm⁻¹.

[b] Indicates a single observed line assigned to two NH_2 transitions. These data were given a relative weight of 0.2 in the least-squares fits.

TABLE I—*Continued*

F	N	K_a	K_c ←	F	N	K_a	K_c	OBSERVED	O-C
1	6	4	2	1	6	5	1	1423.1307	6
2	7	3	5	2	7	4	4	1424.9931	2
2	6	2	5	2	6	3	4	1425.0529	4
1	7	3	5	1	7	4	4	1425.1205	0
1	6	2	5	1	6	3	4	1425.2015	-3
1	3	1	3	1	4	0	4	1427.8710	3
2	3	1	3	2	4	0	4	1427.9288	3
2	6	3	4	2	6	4	3	1427.9589	-1
1	6	3	4	1	6	4	3	1428.1142	1
2	5	3	3	2	5	4	2	1429.3317	0
1	5	3	3	1	5	4	2	1429.5210	-2
2	4	3	2	2	4	4	1	1429.7008	-2
1	4	3	2	1	4	4	1	1429.9358	-1
2	5	0	5	2	5	1	4	1430.8964	2
2	4	3	1	2	4	4	0	1430.9576	2
1	5	0	5	1	5	1	4	1431.0205	0
1	4	3	1	1	4	4	0	1431.1986	1
2	5	2	4	2	5	3	3	1432.7509	1
1	5	2	4	1	5	3	3	1432.9285	-2
2	4	1	4	2	4	2	3	1433.5385	1
1	4	1	4	1	4	2	3	1433.7571	2
1	5	3	2	1	5	4	1	1433.9681	2
2	7	1	6	2	7	2	5	1434.1192	-3
1	7	1	6	1	7	2	5	1434.1626	4
2	2	0	2	2	3	1	3	1434.6714	-3
1	2	0	2	1	3	1	3	1434.7329	0
2	4	2	3	2	4	3	2	1437.9618	7
1	4	2	3	1	4	3	2	1438.1817	-2
2	6	3	3	2	6	4	2	1438.8977	7
1	6	3	3	1	6	4	2	1439.0728	2
2	3	2	2	2	3	3	1	1440.9430	7
1	3	2	2	1	3	3	1	1441.2217	-1
1	3	2	2	1	4	1	3	1441.6116	3
2	3	2	2	2	4	1	3	1441.9218	2
2	3	1	3	2	3	2	2	1444.5048	2
1	3	1	3	1	3	2	2	1444.7626	1
2	7	3	4	2	7	4	3	1445.7323	-5
1	7	3	4	1	7	4	3	1445.8801	7
2	3	2	1	2	3	3	0	1446.3982	7
1	3	2	1	1	3	3	0	1446.6912	-2
1	2	1	2	1	3	0	3	1447.7002	0
2	2	1	2	2	3	0	3	1447.8094	6
2	1	0	1	2	2	1	2	1449.0711	-3
1	1	0	1	1	2	1	2	1449.1832	0
2	4	0	4	2	4	1	3	1449.7150	0
1	4	0	4	1	4	1	3	1449.8169	2
2	6	1	5	2	6	2	4	1450.1532	-2
1	6	1	5	1	6	2	4	1450.2023	-1
2	4	2	2	2	4	3	1	1451.4394	3
1	4	2	2	1	4	3	1	1451.6590	0
2	8	3	5	2	8	4	4	1452.1163	5
1	8	3	5	1	8	4	4	1452.2255	-3
2	8	2	6	2	8	3	5	1452.3861	1
1	8	2	6	1	8	3	5	1452.4146	1
2	2	1	2	2	2	2	1	1452.7053	6
1	2	1	2	1	2	2	1	1453.0458	1
2	5	2	3	2	5	3	2	1456.8303	0
1	5	2	3	1	5	3	2	1456.9902	0
2	7	2	5	2	7	3	4	1458.8226	-3
1	7	2	5	1	7	3	4	1458.8845	-7
2	6	2	4	2	6	3	3	1459.9633	-3
1	6	2	4	1	6	3	3	1460.0710	0
2	5	1	4	2	5	2	3	1461.5076	-2
1	5	1	4	1	5	2	3	1461.5786	0
2	3	0	3	2	3	1	2	1465.1819	0
1	3	0	3	1	3	1	2	1465.2988	2
1	0	0	0	2	1	1	1	1465.3124	-4
1	0	0	0	1	1	1	1	1465.5440	0
2	2	1	1	2	2	2	0	1466.6385	2
1	2	1	1	1	2	2	0	1466.9172	0
2	4	1	3	2	4	2	2	1467.5272	-1
1	4	1	3	1	4	2	2	1467.6379	0
1	2	2	1	1	3	1	2	1468.5876	0
2	3	1	2	2	3	2	1	1468.8051	0
1	3	1	2	1	3	2	1	1468.9766	1
2	2	2	1	2	3	1	2	1469.0641	-2
1	1	1	1	1	2	0	2	1469.1535	0
2	1	1	1	2	2	0	2	1469.3985	5
2	2	0	2	2	2	1	1	1475.7814	-1
1	2	0	2	1	2	1	1	1475.9242	1
1	1	0	1	2	1	1	0	1481.6465	2
2	1	0	1	2	1	1	0	1481.6812	-5
1	1	0	1	1	1	1	0	1481.9116	0
2	1	0	1	1	1	1	0	1481.9471	0
1	3	3	1	1	4	2	2	1483.3794	11
2	3	3	1	2	4	2	2	1484.0497	-20
2	4	3	1	2	5	2	4	1484.4153	-2
2	2	2	0	2	3	1	3	1498.6408	-8
2	3	1	3	2	2	2	0	1506.5130	12
1	3	1	3	1	2	2	0	1506.8860	-2
1	1	1	0	2	1	0	1	1515.1047	-2
1	1	1	0	1	1	0	1	1515.1384	0
2	1	1	0	2	1	0	1	1515.4432	3
2	1	1	0	1	1	0	1	1515.4765	0
1	2	1	1	1	2	0	2	1521.5436	2
2	2	1	1	2	2	0	2	1521.7350	2
2	2	0	2	2	1	1	1	1527.5157	-3
1	2	0	2	1	1	1	1	1527.6856	-1
1	1	1	1	1	0	0	0	1531.1965	-1
2	1	1	1	2	0	0	0	1531.4986	6
1	3	1	2	1	3	0	3	1532.8468	4
2	3	1	2	2	3	0	3	1533.0053	1
1	3	2	1	1	3	1	2	1537.7541	3
2	3	1	2	2	2	2	1	1537.9009	-1
2	3	2	1	2	3	1	2	1538.0662	2
1	3	1	2	1	2	2	1	1538.1915	-2
2	5	2	4	2	4	3	1	1539.1717	6
1	2	2	0	1	2	1	1	1539.2770	0
2	4	2	2	2	3	3	1	1539.3267	6
1	5	2	4	1	4	3	1	1539.4241	0
1	4	2	2	1	3	3	1	1539.6824	-15
1	4	2	2	1	4	1	3	1540.0739	5
1	2	1	2	1	1	0	1	1547.3344	0
2	2	1	2	2	1	0	1	1547.4889	3
1	5	2	3	1	5	1	4	1547.8616	3
2	5	2	3	2	5	1	4	1548.0325	3
2	3	0	3	2	2	1	2	1548.9747	-3
1	3	0	3	1	2	1	2	1549.0362	0
1	4	1	3	1	4	0	4	1549.1839	3
2	4	1	3	2	4	0	4	1549.3414	1
1	2	2	1	1	2	1	2	1552.3248	-2
2	2	2	1	2	2	1	2	1552.8572	-1
1	3	2	2	1	3	1	3	1560.3438	1
2	3	2	2	2	3	1	3	1560.7424	-1
1	3	1	3	1	2	0	2	1561.5127	2
2	3	1	3	2	2	0	2	1561.6086	4
2	6	3	3	2	6	2	4	1564.3684	1
1	4	1	3	1	3	2	2	1566.0754	1
2	4	0	4	2	3	1	3	1568.5356	-3
1	4	0	4	1	3	1	3	1568.5491	0
1	4	3	1	1	4	2	2	1571.3464	2
1	4	1	4	1	3	0	3	1575.1784	3
2	4	1	4	2	3	0	3	1575.2384	0
1	3	3	1	1	3	2	2	1581.8166	7
2	3	3	1	2	3	2	2	1582.4421	2
1	5	2	4	1	5	1	5	1584.0348	-1
2	5	2	4	2	5	1	5	1584.3330	-3
1	2	2	1	1	1	1	0	1585.0531	-1
1	4	3	2	1	4	2	3	1585.1164	-5
2	2	2	1	2	1	1	0	1585.4677	0
2	4	3	2	2	4	2	3	1585.6059	8
1	5	0	5	1	4	1	4	1586.2502	4

TABLE I—*Continued*

F	N	K_a	K_c ←	F	N	K_a	K_c	OBSERVED	O-C	F	N	K_a	K_c ←	F	N	K_a	K_c	OBSERVED	O-C
1	5	1	5	1	4	0	4	1589.3328	0	2	3	3	1	2	2	2	0	1644.4487	-2
2	5	1	5	2	4	0	4	1589.3731	1	1	3	3	0	1	2	2	1	1645.4057	5
1	6	1	5	1	6	0	6	1589.6819	-4	2	3	3	0	2	2	2	1	1645.9114	-7
2	6	1	5	2	6	0	6	1589.8884	9	1	9	0	9	1	8	1	8	1648.2551	7
1	5	3	3	1	5	2	4	1590.7649	0	2	9	0	9	2	8	1	8	1648.2799	6
1	2	2	0	1	1	1	1	1591.0385	0	1	9	1	9	1	8	0	8	1648.3434	1
2	5	3	3	2	5	2	4	1591.1665	-2	2	9	1	9	2	8	0	8	1648.3682	-2
2	2	2	0	2	1	1	1	1591.4860	0	1	7	2	6	1	6	1	5	1652.0292	-4
2	5	1	4	2	4	2	3	1593.1377	-7	2	7	2	6	2	6	1	5	1652.1427	-2
1	5	1	4	1	4	2	3	1593.2156	5	1	4	2	2	1	3	1	3	1658.8064	6
1	3	2	2	1	2	1	1	1601.5349	0	2	4	2	2	2	3	1	3	1659.1263	0
2	3	2	2	2	2	1	1	1601.8522	-2	1	8	1	7	1	7	2	6	1660.0521	5
1	6	0	6	1	5	1	5	1602.6911	0	2	8	1	7	2	7	2	6	1660.0958	6
2	6	0	6	2	5	1	5	1602.7082	-2	1	4	3	2	1	3	2	1	1662.6696	12
1	6	1	6	1	5	0	5	1604.0149	0	1	10	0	10	1	9	1	9	1662.6866	-4
2	6	1	6	2	5	0	5	1604.0452	-1	2	10	0	10	2	9	1	9	1662.7130	0
1	4	2	3	1	3	1	2	1615.5834	-2	2	4	3	2	2	3	2	1	1663.1052	1
2	4	2	3	2	3	1	2	1615.8270	-6	2	8	2	6	2	7	3	5	1664.3523	-3
2	6	1	5	2	5	2	4	1618.1794	1	1	8	2	6	1	7	3	5	1664.3991	1
1	6	1	5	1	5	2	4	1618.1993	1	1	4	3	1	1	3	2	2	1669.7840	2
1	7	0	7	1	6	1	6	1618.3488	0	2	4	3	1	2	3	2	2	1670.2128	0
2	7	0	7	2	6	1	6	1618.3701	-2	1	5	3	3	1	4	2	2	1678.2019	2
1	7	1	7	1	6	0	6	1618.8940	-1	2	5	3	3	2	4	2	2	1678.5734	-5
2	7	1	7	2	6	0	6	1618.9201	-3	1	9	2	8	1	8	1	7	1680.7774	0
1	5	2	4	1	4	1	3	1627.8384	0	2	9	2	8	2	8	1	7	1680.8571	-3
2	5	2	4	2	4	1	3	1628.0374	1	1	5	3	2	1	4	2	3	1697.9935	-2
1	8	0	8	1	7	1	7	1633.4936	-1	1	7	3	5	1	6	2	4	1701.0208	3
2	8	0	8	2	7	1	7	1633.5172	0	2	7	3	5	2	6	2	4	1701.2888	10
1	8	1	8	1	7	0	7	1633.7142	0	1	4	4	1	1	3	3	0	1704.0262	-11
2	8	1	8	2	7	0	7	1633.7395	1	1	4	4	0	1	3	3	1	1704.2673	0
1	6	2	5	1	5	1	4	1639.5386	-1	2	4	4	1	2	3	3	0	1704.5868	13
2	6	2	5	2	5	1	4	1639.6848	-7	2	4	4	0	2	3	3	1	1704.8348	16
2	7	1	6	2	6	2	5	1640.3818	-7	1	5	4	2	1	4	3	1	1724.9056	-14
1	3	3	1	1	2	2	0	1643.9403	7	2	5	4	2	2	4	3	1	1725.4039	-2

IV. ANALYSIS

The Hamiltonian used in the present analysis consists of the A-reduced asymmetric rotor formulation of Watson (*23*) plus the spin–rotation Hamiltonian of Brown and Sears (*24*). All rotational parameters through sextic were included plus the leading eighth-power term (L_K), as well as spin–rotation terms through the quartic. The Hamiltonian was thus identical to that adopted by Birss and co-workers (*4*, *5*), except that we followed the original definition (*24*) for the signs of the spin–rotation centrifugal distortion terms. Note that the spin–rotation parameters denoted here by A^S, B^S, and C^S are identical to the customary parameters ϵ_{aa}, ϵ_{bb}, ϵ_{cc}.

Prior to the present work, information on NH_2 energy levels in the excited ν_2 state has come from electronic spectroscopy (*4*, *5*), from LMR spectroscopy (*10*, *11*), and from some unpublished diode laser measurements (*5*). Information on the ground vibrational state has been obtained from these same sources (primarily the electronic spectrum) and also from microwave-optical double-resonance (MODR) experiments (*25*), far-infrared LMR spectroscopy (*26*), and direct millimeter-wave absorption (*27*). All of these data sources (except for *27*) were used with appropriate weights by Birss *et al.* (*5*) in their large least-squares analyses. As a result, their parameters for the $(v_1v_2v_3)$ = (000) and (010) vibrational states constituted the best available for NH_2. (The (020) state was also analyzed in Ref. (*5*), the (030) state in Ref. (*7*), and many higher vibrational states in Ref. (*8*).)

The first analysis of our new NH_2 data thus involved a direct comparison with line positions calculated from the parameters of Birss *et al.* (*5*). Such a calculation resulted in an rms deviation of 0.0054 cm^{-1} for the 336 lines in Table I. Although this level of agreement was actually quite respectable, it is still more than 10 times greater than our estimated experimental uncertainty. The next level of analysis was to vary the excited (010) vibrational state parameters while keeping the ground (000) state parameters fixed at their values from (*5*); this resulted in an rms deviation of 0.0011 cm^{-1}, which represented a significant improvement although still not matching the experimental uncertainty. Finally, by varying both the (010) and (000) state parameters it was possible to achieve an rms deviation of 0.00044 cm^{-1} for the data of Table I, essentially matching the estimated uncertainty.

We report here the results of the two least-squares fits since we feel that both may be significant. Table II lists the results of the first fit, in which the ground state param-

TABLE II

Parameters (in cm^{-1}) for the (010) Vibrational State of NH_2, Obtained from the Present Data with (000) State Parameters Fixed at the Indicated Values from Ref. (*5*)

	(000)[a]	(010)[b]
ν_0		1497.3184(7)
A	23.6930140	25.968104(438)
B	12.9520477	13.110808(185)
C	8.1726712	8.033752(104)
Δ_K	0.0219407	0.035686(71)
$10^2\ \Delta_{NK}$	-0.416128	-0.54355(209)
$10^2\ \Delta_N$	0.105514	0.117603(347)
$10^2\ \delta_K$	0.100446	0.24808(273)
$10^3\ \delta_N$	0.42539	0.48468(215)
$10^3\ H_K$	0.06280	0.16116(297)
$10^4\ H_{KN}$	-0.1062	-0.2655(134)
$10^6\ H_{NK}$	-0.810	0.952(473)
$10^6\ H_N$	0.4048	0.5306(398)
$10^4\ h_K$	0.1688	0.4146(154)
$10^6\ h_{NK}$	-0.143	-0.109(307)
$10^6\ h_N$	0.2245	0.2711(208)
$10^6\ L_K$	-0.140	-0.421[c]
A^S	-0.3090315	-0.40348(94)
B^S	-0.045185	-0.048217(631)
$10^3\ C^S$	0.4059	0.742(382)
$10^2\ \Delta^S_K$	0.10445	0.2036(99)
$10^3\ \Delta^S_{KN}$	-0.1085	-0.1443(506)
$10^5\ \Delta^S_{NK}$	0.364	0.364[c]
$10^4\ \Delta^S_N$	0.1066	0.1597(709)
$10^4\ \delta^S_K$	0.209	1.030(504)
$10^5\ \delta^S_N$	0.530	0.816(395)

[a] Birss, Merienne-Lafore, Ramsay, and Vervloet (5).
[b] Present result with (000) state fixed at the Ref. (5)values. Uncertainties in parentheses are 3 σ from the least-squares fit.
[c] Fixed at this value from Ref.(5)(see text).

eters were constrained to the values from Ref. (*5*), and Table III lists the results of the second fit, in which ground and excited state parameters were varied. In both fits, the parameters L_K and Δ^S_{NK} were held fixed at values from Ref. (*5*), since they were better determined by the wider range of K_a values fitted in Ref. (*5*). We wished to take full advantage of the inherent precision and self-consistency of the Bomem measurements and thus chose not to incorporate the LMR data for the ν_2 (*10, 11*) or ground states (*26*) into the fits since they are no more precise than our FTS data and do not cover a significantly wider range of N and K_a values. However, for the second fit the present ν_2-band data were supplemented with 28 precise hyperfine-averaged MODR transitions for the ground state (*24, 25*), which were given a relative weight of 100 to reflect their higher precision. The MODR data served to constrain the determination of the ground state spin–rotation parameters in Table III, which thus show little change from the values of Ref. (*5*). The residuals (observed minus calculated wavenumber) from the second fit are listed in Table I for each observed ν_2-band transition.

TABLE III

Parameters (in cm^{-1}) for the (010) and (000) Vibrational States of NH_2 Obtained from the Fit of the Present Data and the MODR Data of Ref. (*23*)[a]

	(000)	(010)
ν_0		1497.3184(3)
A	23.692993(137)	25.968015(209)
B	12.952008(88)	13.110845(101)
C	8.172737(55)	8.033726(56)
Δ_K	0.0219529(143)	0.0356763(317)
$10^2\ \Delta_{NK}$	-0.41603(77)	-0.54270(105)
$10^2\ \Delta_N$	0.105821(189)	0.117895(202)
$10^2\ \delta_K$	0.09943(97)	0.24783(136)
$10^3\ \delta_N$	0.42516(107)	0.48598(114)
$10^3\ H_K$	0.06243(54)	0.16083(132)
$10^4\ H_{KN}$	-0.0941(54)	-0.2593(64)
$10^6\ H_{NK}$	-1.169(158)	0.851(232)
$10^6\ H_N$	0.4334(211)	0.5544(227)
$10^4\ h_K$	0.1511(51)	0.4012(78)
$10^6\ h_{NK}$	-0.071(112)	-0.030(158)
$10^6\ h_N$	0.2162(107)	0.2778(114)
$10^6\ L_K$	-0.140[b]	-0.421[b]
A^S	-0.308897(116)	-0.403393(419)
B^S	-0.045214(55)	-0.048185(278)
$10^3\ C^S$	0.404(34)	0.716(168)
$10^2\ \Delta^S_K$	0.10067(181)	0.20216(449)
$10^3\ \Delta^S_{KN}$	-0.1065(82)	-0.1572(231)
$10^5\ \Delta^S_{NK}$	0.364[b]	0.364[b]
$10^4\ \Delta^S_N$	0.1108(72)	0.1604(319)
$10^4\ \delta^S_K$	0.213(75)	0.916(235)
$10^5\ \delta^S_N$	0.552(38)	0.826(436)

[a] Uncertainties in parentheses are 3 σ from the least-squares fit.

[b] Fixed at this value from Ref.(5) (see text).

It is probable that the (010) state parameters presented here (in Tables II or III) represent a significant improvement over the best previous (*5*) values, thanks to the precision, completeness, and self-consistency of our ν_2-band data. However, the situation with regard to the (000) ground vibrational state is not as clear-cut: our results, in the first column of Table III, are not necessarily better than those of Ref. (*5*), since a very wide variety of high-quality data contributed to that analysis. What is clear is that the parameters in Table III give a substantially better representation than previously available for the ν_2 band, over the range of rotational quantum numbers ($N < 11$ and $K_a < 6$) that are involved in the 350 or so strongest lines in the band at room temperature. Over a wider range of N and K_a values, it is possible that the (000) state parameters of Birss *et al.* (*5*) still give the better representation of the ground state energy levels.

The considerations mentioned in the previous paragraph explain why the results of the two separate least-squares fits (Tables II and III) are given in this paper. More generally, the problems of accurately fitting the rotational energy levels of light asymmetric rotor molecules are well known from the case of water vapor. It is interesting to note that 36 rotational parameters (as compared to the 16 employed here) were required in order to represent the (000) vibrational state of H_2O up to values of $N < 14$ and $K_a < 7$ with an accuracy of 0.0002 cm^{-1} (*28*). Neither our result nor that of Ref. (*5*) even approaches this level of precision and coverage.

V. CONCLUSIONS

Our results may be compared with some recent measurements reported by Krivtsun *et al.* (*12*), who used a pulsed tunable diode laser spectrometer and flash photolysis production to observe 19 transitions in the ν_2 band of NH_2. Seventeen of their observed transitions were observed in the present work (Table I), and the rms deviation between the two sets of measurements is 0.018 cm^{-1}. This deviation is considerably larger than the reported accuracy of either their (0.005 cm^{-1}) or our (0.0004 cm^{-1}) results.

In conclusion, we have observed the ν_2 band of the NH_2 radical with a high-resolution Fourier transform spectrometer and have measured 336 rotational transitions with an accuracy of about 0.0004 cm^{-1}. Two least-squares fits of these data were performed. The first, in which ground vibrational state parameters were fixed at previously reported (*5*) values while (010) state parameters were adjusted, resulted in an rms deviation of 0.0011 cm^{-1}. The second, in which both the (000) and (010) state parameters were adjusted, resulted in an improved deviation of 0.00044 cm^{-1}. Although the second analysis gives the better representation of the ν_2 band for all transitions with significant strength at room temperature, the first analysis may still have more validity for a wider range of rotational quantum numbers. However, neither set of parameters can be expected to predict with accuracy the NH_2 energy levels for values of K_a much greater than those considered here ($K_a = 5$) or in Ref. (*5*) ($K_a = 8$). Our results should be of value for future experiments where the ν_2 band is used for remote observation or for concentration monitoring of the NH_2 radical.

ACKNOWLEDGMENTS

We are grateful to M. Vervloet for helpful discussions, to D. A. Ramsay for his comments on the manuscript, and to D. Janzen for help with the analysis. The work at NOAA was supported in part by the Chemical

Manufacturers Association Technical Panel on Fluorocarbon Research and by the National Aeronautics and Space Administration Upper Atmosphere and Space Services Program.

RECEIVED: August 3, 1987

REFERENCES

1. K. DRESSLER AND D. A. RAMSAY, *Philos. Trans. R. Soc. London, Ser. A* **251,** 553-602 (1959).
2. J. W. C. JOHNS, D. A. RAMSAY, AND S. C. ROSS, *Canad. J. Phys.* **54,** 1804-1814 (1976).
3. M. VERVLOET, M.-F. MERIENNE-LAFORE, AND D. A. RAMSAY, *Chem. Phys. Lett.* **57,** 5-7 (1978).
4. F. W. BIRSS, D. A. RAMSAY, S. C. ROSS, AND C. ZAULI, *J. Mol. Spectrosc.* **78,** 344-346 (1979).
5. F. W. BIRSS, M.-F. MERIENNE-LAFORE, D. A. RAMSAY, AND M. VERVLOET, *J. Mol. Spectrosc.* **85,** 493-495 (1981).
6. M. VERVLOET AND M.-F. MERIENNE-LAFORE, *Canad. J. Phys.* **60,** 49-55 (1982).
7. M.-F. MERIENNE-LAFORE AND M. VERVLOET, *J. Mol. Spectrosc.* **108,** 160-162 (1984).
8. M. VERVLOET, *Mol. Phys.,* in press.
9. D. E. MILLIGAN AND M. E. JACOX, *J. Chem. Phys.* **43,** 4487-4493 (1965).
10. K. KAWAGUCHI, C. YAMADA, E. HIROTA, J. M. BROWN, J. BUTTENSHAW, C. R. PARENT, AND T. J. SEARS, *J. Mol. Spectrosc.* **81,** 60-72 (1980).
11. G. W. HILLS AND A. R. W. MCKELLAR, *J. Mol. Spectrosc.* **74,** 224-227 (1979).
12. V. M. KRIVTSUN, B. B. NADEZHDIN, A. D. BRITOV, I. I. ZASAVITSKII, AND A. P. SHOTOV, *Opt. Spectrosc. (USSR)* **60,** 720-721 (1986).
13. T. AMANO, P. F. BERNATH, AND A. R. W. MCKELLAR, *J. Mol. Spectrosc.* **94,** 100-113 (1982).
14. T. DREIER AND J. WOLFRUM, *Appl. Phys. B* **33,** 213-218 (1984).
15. J. B. BURKHOLDER, P. D. HAMMER, C. J. HOWARD, AND A. R. W. MCKELLAR, *J. Mol. Spectrosc.* **118,** 471-480 (1986).
16. J. B. BURKHOLDER, P. D. HAMMER, C. J. HOWARD, A. G. MAKI, G. THOMPSON, AND C. CHACKERIAN, *J. Mol. Spectrosc.* **124,** 139-161 (1987).
17. A. R. W. MCKELLAR, J. B. BURKHOLDER, A. SINHA, AND C. J. HOWARD, *J. Mol. Spectrosc.* **125,** (1987).
18. J. B. BURKHOLDER, P. D. HAMMER, AND C. J. HOWARD, *J. Phys. Chem.* **91,** 2136-2144 (1987).
19. J. S. WELLS, D. A. JENNINGS, A. HINZ, J. S. MURRAY, AND A. G. MAKI, *J. Opt. Soc. Amer. B* **2,** 857-861 (1985).
20. L. R. BROWN AND R. A. TOTH, *J. Opt. Soc. Amer. B* **2,** 842-856 (1985).
21. W. HACK, H. SCHACKE, H. SCHROTER, AND H. G. WAGNER, "17th Symp. (Int.) Combust.," The Combust. Inst., pp. 505-513, 1979.
22. R. LESCLAUX, *Rev. Chem. Intermed.* **5,** 347-392 (1984).
23. J. K. G. WATSON, *in* "Vibrational Spectra and Structure" (J. R. Durig, Ed.), Vol. 6, pp. 1-89, Dekker, New York, 1977.
24. J. M. BROWN AND T. J. SEARS, *J. Mol. Spectrosc.* **75,** 111-133 (1979).
25. See J. M. COOK, G. W. HILLS, AND R. F. CURL, *J. Chem. Phys.* **67,** 1450-1461 (1977); G. W. HILLS, R. S. LOWE, J. M. COOK AND R. F. CURL, *J. Chem. Phys.* **68,** 4073-4076 (1978); and references therein.
26. P. B. DAVIES, D. K. RUSSELL, B. A. THRUSH, AND H. E. RADFORD, *Proc. R. Soc. London, Ser. A* **353,** 299-318 (1977).
27. A. CHARO, K. V. L. N. SASTRY, E. HERBST, AND F. DE LUCIA, *Astrophys. J. (Lett.)* **244,** L111-L112 (1981).
28. J. W. C. JOHNS, *J. Opt. Soc. Amer. B* **2,** 1340-1354 (1985).