NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (7), 2005—2006 (1976)

The Franck-Condon Factor of the $\tilde{A}$-$\tilde{X}$ System of Ammonia

Isao Kanesaka, Mami Usui, and Kiyoyasu Kawai
Faculty of Literature and Science, Toyama University, Gofuku, Toyama 930

(Received December 6, 1975)

Synopsis. The relative intensity of the $\tilde{A}$-$\tilde{X}$ system of ammonia was calculated by using the harmonic and devised harmonic wave functions. The calculated relative intensities do not agree completely with the observed ones. The relative intensity of the vibronic transition was also calculated. However further improvement was not obtained.

We reported an advanced method[1)] for the calculation of the Franck-Condon factor of a polyatomic molecule and its application to the A-$\tilde{X}$ system of acetylene and dideuterioacetylene. Since the method might be utilized in other systems, it is desirable to clarify the extent of its potentiality. In the present paper we report on the calculated relative intensities of the A-$\tilde{X}$ system of NH_3 and ND_3.

The molecular structure of ammonia in the first excited state[2)] is planar, having D_{3h} symmetry, with an N-H distance of 1.08 Å; that in the ground state[3)] is pyramidal, having C_{3v} symmetry, with an N-H distance of 1.012 Å and an H-N-H angle of 106.7°. The long progressions of the A-$\tilde{X}$ system of NH_3[4)] and ND_3[2)] are represented in cm^{-1} by

$$\nu_{NH_3} = 46136 + 874v_2' + 4v_2'^2$$

$$\nu_{ND_3} = 46714 + 650v_2' + 4v_2'^2.$$

The frequency of 874[4)] or 650[2)] cm^{-1} has been assigned to the out-of-plane bending vibration ν_2' in the first excited state. The observed intensities relative to the 0-0 transition, which are directly estimated from the references,[5,6)] are given in Table 1.

Ammonia in the ground state has a double minimum potential. This causes the splitting of vibrational levels. However, the Franck-Condon factor can be calculated with a high approximation without taking the double minimum potential into consideration.[1,7)] We thus used the mean value of the two observed frequencies (Table 2).[6,8)]

TABLE 1. OBSERVED AND CALCULATED RELATIVE INTENSITIES OF THE $\tilde{A}$-$\tilde{X}$ SYSTEM OF AMMONIA

v'	NH_3				ND_3		
	Obsd[a)]	Calcd			Obsd[b)]	Calcd	
		[I]	[II]	R_v		[I]	[II]
0	1	1	1	1	1	1	1
1	3.9	6.6	6.5	6.4	4.0	8.3	8.1
2	10	22	21	20	10	34	31
3	17	48	42	41	20	91	75
4	24	77	66	62	35	181	135
5	27	95	83	76	50	277	194
6	30	87	89	80	60	329	240
7	27	81	105	94	80	357	302
8	26	32	85	75	110	227	307
9	21	4.4	62	55	160	83	297
10	16	0.12	41	37	200	8.2	278
11	11	0.65	25	24	160	1.8	258

a) From Ref. 5. b) From Ref. 6.

TABLE 2. FUNDAMENTAL FREQUENCIES OF AMMONIA IN THE GROUND STATE

Species		NH_3		ND_3	
		Obsd	$\Delta\nu$[a)]	Obsd	$\Delta\nu$[a)]
A_1	ν_1	3336.7	−3.1	2419.0	−3.4
	ν_2	950.4	0.0	748.8	0.0
E	ν_3	3443.8	3.0	2555.0	3.3
	ν_4	1627.5	0.0	1191.0	0.0

a) $\nu_{obsd} - \nu_{calcd}$. (cm^{-1})

The normal frequencies of NH_3 and ND_3 in the ground state were calculated by the method given by Shimanouchi,[9)] by assuming a simplified force field with an interaction force constant between the bending coordinates. The difference between the observed and calculated frequencies can be seem in Table 2. The force constants are given in Table 3. The small difference between the force constants of NH_3 and ND_3 would scarcely affect the Franck-Condon factor.[1)] The force constants for the out-of-plane bending modes of NH_3 and ND_3 in the excited state are 0.167 and 0.157 mdyn/Å, respectively.

TABLE 3. FORCE CONSTANTS OF AMMONIA IN THE GROUND STATE

	NH_3	ND_3
K(N-X)	6.424	6.484
H(X-N-X)	0.536	0.558
l(X-N-X, X-N-X)	−0.078	−0.071

(X=H or D) (mdyn/Å)

TABLE 4. **L** MATRIX ELEMENTS FOR Z AXIS OF NITROGEN ATOM

	NH_3	ND_3
ν_2'	0.113	0.147
ν_1[a)]	0.0467	0.0682
ν_2[a)]	−0.102	−0.131

a) Designated in Table 2.

The normal coordinate vector of ν_2' is parallel to the C_3 axis. Thus only two normal coordinates of A_1 species in the ground state are taken into consideration. The values of the **L** matrix elements for the nitrogen atoms are given in Table 4. The values of the overlap integral for the nitrogen atoms of NH_3 and ND_3 are 0.0224 and 0.0123, respectively, at $v'=0$, by considering the double minimum potential in the ground state.[1] Those for the hydrogen atom are the same as those for the nitrogen atom. Actually, the overlap integral for the hydrogen atom is two-dimensional, hence smaller than that for the nitrogen atom, and we therefore do not take it into consideration, since the overlap integral perpendicular to the C_3 axis is omitted in our approximation.[1] This scarcely alters the calculated relative intensities. The value of the oscillator-strength of the $\tilde{A}$–$\tilde{X}$ system of NH_3 has been reported to be 0.088.[5] This shows that the value of the observed oscillator-strength, f_v, is 4.42×10^{-5} for the 0 - 0 transition.

Calcd [I] and Calcd [II] were obtained by using the harmonic and devised harmonic[1] wave functions, respectively, in the excited state (Table 1). The calculated relative intensities do not agree completely with the observed ones. In higher levels the results of Calcd [II] are much better than those of Calcd [I]. Though the improvements seem to be satisfactory on the basis of our assumptions, the maxima of the observed and calculated relative intensities do not agree. This may be caused by the vibronic transition given by:

$$R_v(v', 0) = \int \Psi'_{v'} Q \Psi''_0 \mathrm{d}Q$$

where Q is a normal coordinate, and Ψ' and Ψ'' are vibrational wave functions of the excited and ground states, respectively. We thus calculated $R_v(v', 0)$ by our method (Table 1). The variation in results is similar to that of Calcd [II]; similar results were obtained for ND_3. This shows that further improvement can not be expected from the vibronic transition. Precise wave functions for the excited state should be used.

In the present case the treatment of the overlap integral is essentially the same as that for a diatomic molecule, ammonia being one of the simplest molecules. The results given in Table 1 seem to show the limits of the applicability of our method.

References

1) I. Kanesaka and K. Kawai, *Bull. Chem. Soc. Jpn.*, **48**, 2745 (1975).

2) A. E. Douglas, *Discuss. Faraday Soc.*, **35**, 158 (1963).

3) E. D. Palik and E. E. Bell, *J. Chem. Phys.*, **26**, 1093 (1957).

4) A. D. Walsh and P. A. Warsop, *Trans. Faraday Soc.*, **57**, 345 (1961).

5) K. Watanabe, *J. Chem. Phys.*, **22**, 1564 (1954).

6) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton (1966).

7) W. L. Smith and P. A. Warsop, *Trans. Faraday Soc.*, **64**, 1165 (1968).

8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton (1945).

9) T. Shimanouchi, "Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules," Tokyo Univ. Press. (1968).