

Transition dipole moments of NH_3 in excited vibrational states determined by laser Stark spectroscopy

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Ammonia is probably the best known example of a molecule which undergoes inversion. The consequences of this motion are that the degenerate levels of a normal symmetric rotor are split and that the molecule cannot be strictly considered to possess a permanent dipole moment. The so-called ground state dipole moment is really the transition moment between the two inversion levels and this has been measured to be $\langle 0_+ | \mu | 0_- \rangle = 1.4712 \text{ D}$.¹⁻³ The value obtained for the corresponding quantity in the $\nu_2 = 1$ state was $\langle 1_+ | \mu | 1_- \rangle = 1.253 \text{ D}$,³⁻⁵ and the infrared transition moment between the ground and the $\nu_2 = 1$ state was determined to be $\langle 0_+ | \mu | 1_- \rangle = \langle 0_- | \mu | 1_+ \rangle = 0.24 \text{ D}$.⁶ As higher ν_2 modes are excited so that the energy is well above the potential barrier to inversion, the distinction between the inversion motion and the ν_2 vibration is lost and the two types of transition are expected to become very similar in magnitude. A theoretical investigation of the dipole moment function of ammonia has been carried out by Spirko.⁷

The purpose of the work described in this paper was to obtain experimental data on the variation of transition moment with vibrational excitation by carrying out laser Stark spectroscopy measurements in the $2\nu_2^- - \nu_2^+$ hot band. The problem with making such measurements is that the energy separation between the two inversion levels of a particular state increases rapidly with excitation of ν_2 , and consequently the Stark shifts which may be induced in the levels of a particular state decrease rapidly with increasing vibrational quantum number. Thus for the ν_2 fundamental transition the major contribution to the observed Stark shift dominantly comes from the movement of the lower state levels. In the case of the measurement of $\langle 1_+ | \mu | 1_- \rangle$ this problem was overcome by making use of an accidental near degeneracy⁴ or a coincidence of laser line with a $K=0$ transition of the ν_2 fundamental.⁵ Unfortunately no such convenient accident has been found so far in the $2\nu_2^- - \nu_2^+$ hot band and the present measurements were carried out using conventional inverse Lamb-dip Stark spectroscopy.

It was found that Stark components of the $Q(1, 1)$ and $R(4, 3)$ transitions could be brought into coincidence with the $10.4 \mu\text{m}$ $P(14)$ and the $9.4 \mu\text{m}$ $P(24)$ CO_2 laser lines respectively, by applying electric fields up to 90 kV/cm . The frequency separation between these transitions and the relevant laser lines has been determined⁸⁻¹⁰ with relative high accuracy and this allowed the frequency shifts calculated from our data to be checked.

The apparatus used consisted of a CO_2 -laser operating single mode and stabilized at the center of its gain profile and a Stark cell, which has been described pre-

viously,¹¹ in a Lamb-dip configuration. The plane of polarization of the laser beam was set at approximately 45° to the Stark field, so that by adjusting a polarizer in front of the cell a quick change between $\Delta M = \pm 1$ and $\Delta M = 0$ transitions could be made. This was of particular importance in the case of the $Q(1, 1)$ transition, since in this way the field difference between resonance of the $M = 1 - 1$ and $M = 0 - 1$ transition could be accurately measured and this difference is only dependent on the level splittings in the $\nu_2 = 2$ state. The resonant voltages for the $Q(1, 1)$ transition with the $P(14)$ laser line were $M = 1 - 1$, $87630 \pm 220 \text{ V/cm}$; $M = 0 - 1$, $88487 \pm 130 \text{ V/cm}$, and the difference in voltage was measured directly to be $857 \pm 150 \text{ V/cm}$. For the $R(4, 3)$ transition and the $P(24)$ laser line $M = 5 - 4$, $55780 \pm 22 \text{ V/cm}$ and $M = 4 - 3$, $76066 \pm 22 \text{ V/cm}$ were measured. The uncertainties quoted are three times the standard deviation in all cases.

These measurements together with the data available from other sources allowed the magnitude of the transition dipole moments $\langle 3_+ | \mu | 2_- \rangle$ and $\langle 2_+ | \mu | 2_- \rangle$ to be determined. The energy levels and the various transition moments used in the analysis are shown in Fig. 1. The Stark shift of the $\nu_2 = 2_- - 1_-$ infrared transition is composed of a shift of the 2_- state due to the transition moments $\langle 3_+ | \mu | 2_- \rangle$, $\langle 2_+ | \mu | 2_- \rangle$ and $\langle 2_- | \mu | 1_+ \rangle$ and a shift of the 1_- state via transition moments $\langle 2_- | \mu | 1_- \rangle$, $\langle 1_- | \mu | 1_+ \rangle$, and $\langle 1_- | \mu | 0_- \rangle$. Contributions from elements such as $\langle 4_+ | \mu | 2_- \rangle$ and $\langle 2_- | \mu | 0_+ \rangle$ due to anharmonicity and $\langle 2_- | \mu | 1_- \rangle$ due to $\Delta K = \pm 3$ matrix elements¹² were found to be negligible. We also checked that the contribution of the Coriolis mixing between the $2\nu_2$ state and the ν_4 state¹³ is negligible in the present cases. Of the five

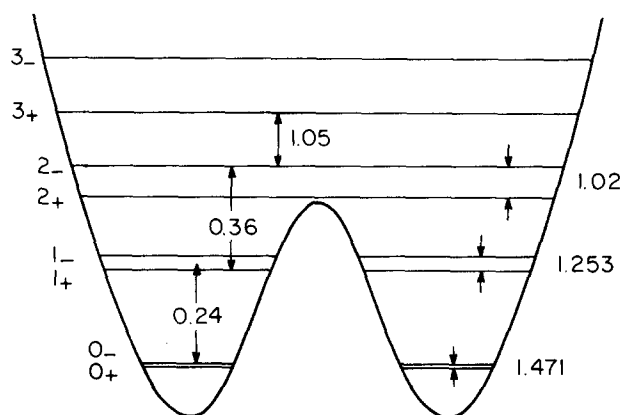


FIG. 1. Vibration-inversion energy levels of NH_3 and observed transition dipole moments in Debye. The transition dipole moment $\langle 0_+ | \mu | 0_- \rangle$, $\langle 1_+ | \mu | 1_- \rangle$, and $\langle 1_+ | \mu | 0_+ \rangle$ were given in Refs. 1-3, 3-5, and 6 respectively. Other three values have been obtained in this work.

dipole moments which were considered the last two have been given^{5,6} and $\langle 2_{-} | \mu | 1_{+} \rangle$ can be determined from the intensity measurement¹⁰ of the $R(4,3)$ transition to be 0.36 ± 0.03 D. Using these three known values and the vibration-rotation energy levels of the 1_{+} and 2_{+} states¹⁴ and the 3_{+} state,¹⁵ under the assumption that the rotational structure of the 3_{+} state is the same as that of the 2_{+} state, the unknown transition dipole moments were determined to be

$$\langle 2_{-} | \mu | 2_{+} \rangle = 1.02 \pm 0.18 \text{ D}$$

and

$$\langle 3_{+} | \mu | 2_{+} \rangle = 1.05 \pm 0.34 \text{ D}.$$

The uncertainties result from the error of measurements mentioned earlier and the uncertainty in the energy levels (especially of 1_{+}). The latter was estimated to be 0.1 cm^{-1} . If we reduce this value to 0.05 cm^{-1} , the uncertainties for the dipole moments are 0.13 and 0.28 D, respectively.

The separation between the $Q(1,1)$ and $R(4,3)$ transitions and the nearby laser lines was calculated to be -977 ± 20 and -473 ± 10 MHz, respectively, which agree to within the quoted error limits with values obtained by other methods.^{8,10}

In a recent theoretical study of the dipole moment function of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$, Spirko^{7,16} has predicted the transition dipole moments given above. The values obtained were

$$\langle 2_{-} | \mu | 2_{+} \rangle = 0.960 \pm 0.002 \text{ D}$$

and

$$\langle 2_{-} | \mu | 3_{+} \rangle = 0.936 \pm 0.003 \text{ D},$$

which can be seen to be in excellent agreement with our experimental values.

Thus we have confirmed the classical contention that the vibrational transition dipole moment of NH_3 is of the order of the "ground state" dipole moment above the barrier of inversion. This must apply also to other molecules in highly excited vibrational states such as those considered in infrared-laser-induced molecular dissociation.^{17,18} It is quite possible for molecules with certain shape that the transition moments in the excited

states increase more rapidly because of inversion than the normally considered matrix element of $(v+1)^{1/2}$.

Note added in proof: C. K. Rhodes has drawn our attention to an earlier measurement of NH_3 transition dipole moments (W. K. Bischel, P. J. Kelly, and C. K. Rhodes, *Phys. Rev. A* **13**, 1829 (1976)). They obtained $\langle 1_{+} | \mu | 2_{-} \rangle = 0.27 \pm 0.05$ D and $\langle 2_{+} | \mu | 2_{-} \rangle = 0.83 \pm 0.08$ D by using an A. C. Stark shift and a D. C. Stark shift, respectively, of two-photon transitions. The discrepancy between their value of $\langle 2_{+} | \mu | 2_{-} \rangle$ and ours is probably due to their neglect of $\langle 3_{+} | \mu | 2_{-} \rangle$ in the analysis.

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