# Direct measurements of transition dipole matrix elements using optical nutation

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We describe a method of directly determining transition dipole matrix elements which we have used to make the first measurements of this quantity in an asymmetric rotor. A low pressure gas (a few mtorr NH<sub>2</sub>D) which is subjected to a cw CO<sub>2</sub> laser beam is suddenly Stark switched into resonance. An optical nutation signal is detected whose frequency yields  $\mathcal{P}_{e}/\hbar$ , where  $\mathcal{P}$  is the transition dipole matrix element of interest and  $E_0$  is the optical field strength which may be determined from power and beam profile measurements. Thus an observation of the nutation frequency along with the power measurements yields  $\mathcal{P}$  This was done for two transitions of NH<sub>2</sub>D giving transition dipole matrix elements along two axes in the molecule:  $\langle v_2 = 0_d (\partial \mu_a / \partial Q) Q | v_2 = 1_a \rangle = 0.112 \pm 0.009$  D and  $\langle 0_d (\partial \mu_e / \partial Q) Q | 1_s \rangle = 0.158 \pm 0.009$  D. The extension of this technique to nonpolar molecules and its advantages over conventional steady state laser methods are discussed.

## I. INTRODUCTION

An important parameter in any spectroscopic experiment is the transition dipole matrix element,  $\mathcal{P} = \int \psi_a^* \sum_i \\ \times e_i r_i \psi_b d\tau$ , since it is  $|\mathcal{P}|^2$  which fundamentally determines the strength of a transition from a state  $\psi_a$  to another state  $\psi_b$ . Accurate values of  $\mathcal{P}$  are useful in a wide variety of applications including the study of population distributions in gases, radiative energy transfer problems, and the search for new laser transitions. In addition, for vibrational transitions in molecules, the vibrational piece of  $\mathcal{P}$  can be used as a test for vibrational potentials and wavefunctions. Thus, accurate methods for measuring  $\mathcal{P}$  are of considerable interest.

In this paper we demonstrate the direct, accurate measurement of transition dipole matrix elements using optical nutation. This phenomenon is seen as a damped oscillation in the transmitted intensity which occurs when a molecular transition is suddenly brought into resonance with a laser beam.<sup>1</sup> The oscillation arises because molecules are driven coherently back and forth between the ground and excited states producing an alternating absorption and emission of radiation. If the transition is excited exactly on resonance by a uniform optical field with amplitude  $E_0$ , the oscillation frequency is just  $\Phi E_0/\hbar$ . Thus, a measurement of the laser intensity  $I = \frac{1}{2} c \epsilon_0 E_0^2$  gives the matrix element directly.

Transition dipole matrix elements can also be determined by a steady state laser method where the absolute absorption as a function of pressure is measured.<sup>2</sup> This method can give accurate results, but only when certain conditions are met. Optical nutation is complementary to the steady state method since the accuracy of the two techniques depends on different parameters, and one can often be used in situations where the other fails. A more detailed comparison of the two techniques is given in Sec. IV. Curve of growth measurements using a conventional ir spectrometer can also provide a determination of  $\mathfrak{G}$ .<sup>3</sup> However, this technique can only be used for the simplest molecules and is not the method of choice if a laser at the proper frequency is available. deuterated ammonia, NH<sub>2</sub>D, using a Stark switching technique described below. Transition dipole matrix elements are obtained for two vibration-rotation transitions in the molecule, and since the transition assignments are known, the vibrational piece of the transition dipole matrix elements along two different axes in the molecule are determined. These quantities should provide a sensitive test of the  $\nu_2$  vibrational wavefunction in NH<sub>2</sub>D.

There has been one previous attempt to measure o using optical nutation by Hocker and Tang, who made a measurement on SF<sub>6</sub> using a pulsed laser.<sup>4</sup> It is hard to assess the accuracy of their results because of the difficulties inherent in this type of experiment. In particular, the optical field strength changes during the pulse and the laser frequency can be chirped, both of which will vary the nutation frequency. It is also difficult to accurately measure the nutation signal that does occur, since it appears as a small signal on the time varying background. Finally, a determination of the optical field strength is extremely difficult since the pulse shape, the pulse energy, and the transverse profile of the beam must all be reproducible and accurately known. Thus, the measurement of transition dipole matrix elements using this approach does not appear very promising if accuracies much beyond a rough estimate are desired.

The difficulties just mentioned can be avoided, however, by using the Stark switching technique. In this method, which we have used for the measurements reported here, a cw laser is utilized, and molecular transitions are shifted in and out of resonance using the Stark effect.<sup>5</sup> Thus, one merely passes the laser beam through the sample and applies a pulsed electric field across it. The optical nutation signal is observed by monitoring the transmitted light with a photodetector. Using a pulsed electric field instead of a pulsed laser produces several significant advantages. First, because the laser beam is cw, it produces only a dc signal in the detector. The only ac signal present is just the optical nutation signal one wants to observe! This allows the nutation signal to be accurately measured. Secondly, since the pulsed electric field can be a nearly

Our optical nutation measurements were made on a

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ideal step function and the cw laser is stable in amplitude and frequency, an exact theoretical calculation of the optical nutation signal can be made with  $\sigma$  as an adjustable parameter. Finally, the laser intensity may be accurately measured by using a calibrated thermopile to obtain the total beam power and a scanning aperture to obtain the beam's transverse intensity profile. Thus, one expects that accurate measurements of  $\sigma$  can be made, and we show that these expectations are fulfilled.

A fundamental limitation of the Stark switching technique is, of course, that transitions with a substantial Stark effect must be used. However, the technique can be generalized by frequency switching the laser instead of the sample. Optical nutation can then be observed in any transition that overlaps a laser line. This point is discussed further in Sec. IV.

## **II. THEORY**

The theory of the optical nutation effect has been discussed by several authors.<sup>6,7</sup> In this section we review the semiclassical treatment of optical nutation in a form suitable for comparison with our experimental results. We wish to consider what happens when a cw laser beam passes through a low pressure gas sample with a resonant, nondegenerate transition. The laser frequency  $\Omega_L$  is assumed initially to be somewhere within the Doppler broadened linewidth of the transition (~ 80 MHz FWHM for NH<sub>2</sub>D at  $\lambda = 10 \ \mu m$ ). Only those molecules with a z component of velocity  $v'_{z}$  such that they are Doppler shifted into resonance are excited, and this narrow velocity group has a homogeneous linewidth which is typically 100 kHz-1 MHz FWHM. At t = 0, a step function electric field is applied across the sample which shifts the center frequency of the transition to a new value. If the frequency shift is several homogeneous linewidths or more, a new velocity group  $v''_{r}$  will suddenly be shifted into resonance producing an optical nutation signal. In addition to the optical nutation, there will also be an optical free induction decay signal (FID) from the velocity group  $v'_{*}$  which was shifted out of resonance.<sup>8</sup> This signal can be ignored in practice because the FID appears as a heterodyne beat with the laser and decays as

$$\exp\left\{-\gamma t - \left[\sqrt{\gamma^2 + (\sigma E_0/h)^2}\right]t\right\},\$$

where  $\gamma = 1/\tau$  is the collisional decay rate.<sup>8</sup> Thus the FID has essentially died out by the end of the first cycle of optical nutation, and even during that cycle, its amplitude can be made negligibly small by simply Stark shifting far enough to make the heterodyne beat frequency lie outside the bandwidth of the detection system. In light of this we may neglect the previously excited velocity group  $v'_{\varepsilon}$ , and consider only the response of an unexcited transition suddenly shifted into resonance at l=0. Our approach will be to calculate the molecular polarization via the density matrix equations of motion, and then to use Maxwell's equations to find the signal which appears at the detector.

We take the optical field to be

$$E_L = E_0 \cos(\Omega_L t - kz)$$

Considering now an ensemble of molecules with axial velocities between  $v_{\mathbf{z}}$  and  $v_{\mathbf{z}} + dv_{\mathbf{z}}$ , and making a (non-relativistic) transformation to a moving coordinate frame in which these molecules are at rest, this becomes

$$E_L = E_0 \cos(\Omega'_L l - kz') , \qquad (2)$$

where  $\Omega'_L = \Omega_L - kv_z$ , and z' is the molecular position in the moving frame. We assume an optically thin sample so that  $E_0$  does not depend on z'. This condition is certainly satisfied in our experiments where the peak absorption is ~ 0.3%.

The equation of motion for the molecular density matrix can be written

$$\dot{\rho} = -\frac{i}{\hbar} \left[ \mathbf{H}, \rho \right] - \frac{1}{\tau} \left( \rho - \rho^0 \right) , \qquad (3)$$

where  $\rho^0$  is the density matrix in thermal equilibrium, and we have introduced a single phenomenological decay time  $\tau$ . This is equivalent to the assumption that the molecular relaxation processes are dominated by strong collisions in which the collisional transition probability to any level is simply proportional to the Boltzmann factor for that level. We could allow the population difference  $\rho_{bb} - \rho_{aa}$  and the relaxation time for the off-diagonal element  $\rho_{ab}$  to have different relaxation times (i.e.,  $T_1 \neq T_2$ ). However, as discussed below in Sec. III, for the high powers and low sample pressures used in our experiments, the decay of the observed optical nutation signal is dominated by effects due to the transverse intensity profile of the laser beam. Thus, the details of the collisional decay model do not significantly affect the results of the calculation, and we will proceed using the simpler strong collision model.9

Denoting the upper state as  $\psi_a$ , the lower state as  $\psi_b$ , and the energy difference between them as  $w_a - w_b = \hbar \omega_0$ , we can write equations of motion for the individual elements of Eq. (3). In the dipole approximation, the Hamiltonian is  $\mathbf{H} = \mathbf{H}_0 - E_L \sum_i e_i \mathbf{r}_i$ , where the summation is over all electrons and nuclei in the molecule. Assuming  $E_L$  to be linearly polarized along the x axis, the matrix elements of  $\mathbf{H}$  are  $\mathbf{H}_{aa} = w_a$ ,  $\mathbf{H}_{bb} = w_b$ , and  $\mathbf{H}_{ab}$  $= \mathbf{H}_{ba}^* = -\langle \psi_a | \sum_i e_i x_i | \psi_b \rangle E_L = - \mathcal{O} E_L$ . Also,  $\rho_{aa}^0 = N_a/N$ ,  $\rho_{bb}^0 = N_b/N$ , where  $N_a$  and  $N_b$  are the thermal equilibrium populations of levels a and b, and  $N = N_a + N_b$ . Thus we obtain

$$\frac{d}{dt} \left(\rho_{bb} - \rho_{aa}\right) = \frac{2i \mathscr{O} E_L}{\hbar} \left(\rho_{ab} - \rho_{ba}\right) + \frac{1}{\tau} \left(\frac{N_b - N_a}{N} - \left(\rho_{bb} - \rho_{aa}\right)\right),$$

$$\frac{d}{dt} \rho_{ab} = \frac{d}{dt} \rho_{ba}^* = \frac{i \mathscr{O} E_L}{\hbar} \left(\rho_{bb} - \rho_{aa}\right) - i \omega_0 \rho_{ab} - \frac{1}{\tau} \rho_{ab}.$$
(4)

The rapidly oscillating component of  $\rho_{ab}$  may be removed by setting

$$\rho_{ab} = \tilde{\rho}_{ab} e^{-i(\Omega'_L t - kz')} . \tag{5}$$

Making this substitution and using the rotating wave approximation, we obtain

(1)

$$\frac{d}{dl} (\rho_{bb} - \rho_{aa}) = 2iy(\tilde{\rho}_{ab} - \tilde{\rho}_{ba}) + \frac{1}{\tau} \left( \frac{N_b - N_a}{N} - (\rho_{bb} - \rho_{aa}) \right) ,$$

$$\frac{d}{dl} \tilde{\rho}_{ab} = iy(\rho_{bb} - \rho_{aa}) - i(\omega_0 - \Omega'_L) \tilde{\rho}_{ab} - \frac{1}{\tau} \tilde{\rho}_{ab} ,$$
(6)

where  $y = \Phi E_0/2\hbar$ . The second equation has both real and imaginary parts since  $\tilde{\rho}_{ab}$  is complex. Thus it is convenient to set

$$\tilde{\rho}_{ab} = \frac{1}{2} \left( R_{\rm I} - i R_{\rm II} \right) \,, \tag{7}$$

$$\rho_{bb} - \rho_{aa} = R_{III} ,$$

which gives

$$\dot{R}_{1} = -(\omega_{0} - \Omega_{L}')R_{11} - (1/\tau)R_{1} , \qquad (8a)$$

$$\dot{R}_{\rm II} = (\omega_0 - \Omega'_L)R_{\rm I} - 2yR_{\rm III} - (1/\tau)R_{\rm II} , \qquad (8b)$$

$$\dot{R}_{\rm III} = 2yR_{\rm II} + (1/\tau)[(N_b - N_a)/N - R_{\rm III}] . \tag{8c}$$

Equations (8) are the optical analogs of the NMR Bloch equations.<sup>10</sup> As discussed earlier, the molecules excited at time l < 0 give rise to a FID and may be ignored. Thus, we consider the molecules to be unexcited at l=0, and we let  $\omega_0$  be the Stark shifted resonant frequency in the moving coordinate system. The boundary conditions on Eqs. (8) are then

$$R_{\rm I}(0) = 0, \quad R_{\rm II}(0) = 0, \quad R_{\rm III}(0) = (N_b - N_a)/N.$$
 (9)

Using Eq. (9), the solution of Eq. (8b) is

$$R_{II}(t) = \frac{N_b - N_a}{N} \left\{ -\frac{y}{g} e^{-t/\tau} \sin 2gt - \frac{2y\tau}{1 + 4g^2\tau^2} \times \left[ 1 - e^{-t/\tau} \left( \cos 2gt + \frac{1}{2g\tau} \sin 2gt \right) \right] \right\}, \quad (10)$$

where  $g = \frac{1}{2} \left[ (\omega_0 - \Omega'_L)^2 + 4y^2 \right]^{1/2}$ . The solution for  $R_I$  can be written

$$R_{\rm I}(t) = e^{-t/\tau} \int_0^t e^{-t'/\tau} (\Omega'_L - \omega_0) R_{\rm II}(t') dt' . \tag{11}$$

The induced polarization per molecule is given by

$$p'(t, v_z) = \sigma(\rho_{ab} + \rho_{ba})$$
$$= \sigma[R_{I}\cos(\Omega'_{L}t - kz') - R_{II}\sin(\Omega'_{L}t - kz')], \quad (12)$$

where the  $v_z$  dependence of p' explicitly takes account of the fact that only a single velocity group of molecules has so far been considered in the calculation.

The polarization of the sample may now be calculated by writing Eq. (12) in terms of laboratory frame quantities and integrating over all velocities  $v_z$ . The number of molecules/cm<sup>3</sup> with  $v_z$  between  $v_z$  and  $v_z + dv_z$  is

$$N(v_z) = \frac{Nke^{-(kv_z)^2/(\Delta\omega_D)^2}dv_z}{\Delta\omega_D\sqrt{\pi}},$$
(13)

where  $\Delta \omega_D = (\omega_0/c)\sqrt{2k_BT/m}$  is the 1/e half-width of the Doppler broadened line profile. The polarization is thus

$$P(t) = \mathcal{O}\frac{N}{\Delta\omega_D\sqrt{\pi}} \int_{-\infty}^{\infty} k \, e^{-(kv_z)^2/(\Delta\omega_D)^2} [R_{\rm I}\cos(\Omega_L t - kz) - R_{\rm II}\sin(\Omega_L t - kz)] \, dv_z \,, \quad (14)$$

where the relation  $\Omega'_L = \Omega_L - kv_z$  is used to express  $R_I$ and  $R_{II}$  in terms of laboratory frame quantities only. Equation (14) can be simplified considerably by allowing the laser frequency to fall at the center of the Doppler curve so that  $\omega_0 = \Omega_L$ . This was the case in our experiments. *g* is then given by

$$g = \frac{1}{2} \left[ (kv_s)^2 + 4y^2 \right]^{1/2} . \tag{15}$$

This makes  $R_{II}$  an even function of  $v_z$  and  $R_I$  an odd function, so that the first term in the integral of Eq. (14) vanishes. Thus

$$P(t) = \left\{ -\sigma \int_{-\infty}^{\infty} N(v_z) R_{II} dv_z \right\} \sin(\Omega_L t - kz)$$
$$\equiv \mathbf{P}(t) \sin(\Omega_L t - kz) , \qquad (16)$$

where P(t) is the polarization amplitude. To calculate the observed signal, we use this polarization in Maxwell's equations to find the optical field emitted by the molecules. Since the polarization in Eq. (16) is assumed to be a plane wave, we may look for a plane wave solution of Maxwell equations,

$$E(t) = \mathsf{E}_{s}(z, t) \cos(\Omega_{L}t - kz) + \mathsf{E}_{s}'(z, t) \sin(\Omega_{L}t - kz) . \tag{17}$$

Furthermore, since the polarization amplitude varies slowly in time compared to an optical period and slowly in space compared to an optical wavelength, the slowly varying envelope approximation can be made, yielding linearized wave equations for the emitted field amplitudes  $\mathbf{E}_{s}(z, t)$  and  $\mathbf{E}'_{s}(z, t)$ ,

$$\left(\frac{\partial}{\partial z} + \frac{1}{c} \frac{\partial}{\partial t}\right) \mathbf{E}_{s}(z, t) = \frac{\Omega_{L}}{2\epsilon_{0}c} \mathbf{P}(t) , \qquad (18a)$$

$$\left(\frac{\partial}{\partial z} + \frac{1}{c} \frac{\partial}{\partial l}\right) \mathbf{E}'_{s}(z, l) = 0 .$$
 (18b)

The right-hand side of Eq. (18b) is zero because a plane wave polarization can only drive a field 90° out of phase with itself. Letting z = 0 be the point where the laser beam enters the sample, we have boundary conditions  $\mathbf{E}_{s}(0, t) = \mathbf{E}'_{s}(0, t) = 0$ . Thus  $\mathbf{E}'_{s}(z, t) = 0$  everywhere. Equation (18a) can be simplified by noting that in our experiments  $\mathbf{E}_{s}$  builds up over a sample length of ~ 30 cm while amplitude variations at a given z occur on a time scale of ~ 0.1  $\mu$ sec. Thus,  $\partial \mathbf{E}_{s}/\partial z \gg (1/c)(\partial \mathbf{E}_{s}/\partial t)$ , so we ignore the  $\partial \mathbf{E}_{s}/\partial t$  term and integrate Eq. (18a) trivially to yield an output field,

$$\mathbf{E}_{s} = -\frac{\Omega_{L}L}{2\epsilon_{0}c} \mathbf{P}(t) , \qquad (19)$$

where L is the length of the sample.

The optical field reaching the detector is a sum of the laser field and the emitted molecular field. Since optical detectors are square law devices, we need to calculate the intensity present at the detector, which is

$$I(t) = c\epsilon_0 \langle [E_0 \cos(\Omega_L t - kz) + \mathbf{E}_s \cos(\Omega_L t - kz)]^2 \rangle_{av}, \quad (20)$$

where the time average is taken over many optical cycles. Thus

$$I(t) = c \epsilon_0 (E_0^2/2 + \mathbf{E}_s E_0 + \mathbf{E}_s^2/2) .$$
<sup>(21)</sup>

Now  $E_s \ll E_0$  for an optically thin sample, so the third term of Eq. (21) may be ignored. Evaluating  $E_s$  from Eqs. (10), (13), (16), and (19), we obtain our final result

$$I(t) = I_0 - \frac{\theta^2 E_0^2 \Omega_L L(N_b - N_a)}{4 \hbar \omega_D \sqrt{\pi}} \int_{-\infty}^{\infty} k \, e^{-(k v_a)^2 / (\Delta \omega_D)^2} \left\{ \frac{1}{R} \, e^{-t/\tau} \sin 2g t - \frac{2\tau}{1 + 4g^2 \tau^2} \left[ 1 - e^{-t/\tau} \left( \cos 2g t + \frac{1}{2g' t} \sin 2g t \right) \right] \right\} \, dv_a \,, \quad (22)$$

where  $I_0 = c \epsilon_0 E_0^2/2$ . In the limit as  $l \to \infty$ , this equation reduces to the standard expression for steady state saturated absorption at the peak of a Doppler broadened line. If the relaxation time  $\tau$  is long, we may obtain an approximate solution for I(t) by setting  $\tau = \infty$ . The integral in Eq. (22) can then be evaluated to give  $2\pi J_0[(\sigma E_0/\hbar)t]$ . Since the zero order Bessel function  $J_0$  is approximately unity for small t, the initial peak value of the optical nutation signal will be

$$\Delta I_{\text{peak}} = -\frac{\vartheta^2 E_0^2 \Omega_L (N_b - N_a) L \sqrt{\pi}}{2 \hbar \omega_D} .$$
 (23)

We note that Eq. (23) is exactly the expression one obtains for *unsaturated* absorption assuming a small optical field. This is not unexpected since for a short time after the molecules are switched into resonance, the level populations have not yet changed appreciably and one sees the full unsaturated absorption.

Equation (22) was derived assuming plane wave excitation. In our experiments, however, the laser beam has a Gaussian profile, which means that  $E_0$  should be replaced by  $E_0 e^{-R^2/2w^2}$  in that equation. Neglecting diffraction effects, the observed signal for a large area detector is then the integral of Eq. (22) over the beam profile,

$$S = 2\pi \int_0^\infty I(t) R \, dR \quad . \tag{24}$$

The integration causes the observed nutation signal to damp more rapidly but does not significantly affect the nutation frequency. This can be seen by using the approximate zero order Bessel function solution in Eq. (24). We have

$$S = \pi w^{2} I_{0} - \frac{\hbar \Omega_{L} L (N_{b} - N_{a}) \pi^{2}}{\Delta \omega_{D} \sqrt{\pi} t^{2}} \int_{0}^{\infty} \frac{\varphi^{2} E_{0}^{2} e^{-R^{2} / w^{2}} t^{2}}{\hbar^{2}} J_{0} \left( \frac{\varphi E_{0} e^{-R^{2} / 2w^{2}}}{\hbar} t \right) R dR = \pi w^{2} \left( I_{0} - \frac{\Omega_{L} L (N_{b} - N_{a}) \sqrt{\pi}}{\Delta \omega_{D}} \left( \varphi E_{0} / t \right) J_{1} \left[ \left( \varphi E_{0} / \hbar \right) t \right] \right).$$
(25)

Inspection of the functions  $J_0(x)$  and  $J_1(x)$  shows that their oscillation "frequencies" are equal to better than 2%, so the integrated signal frequency is essentially the same as the nutation frequency one would obtain if a plane wave of amplitude  $E_0$  had excited the sample. The damping, however, is greater due to the 1/t factor. The exact numerical solutions using Eqs. (22) and (24) behave similarly.

## III. EXPERIMENTAL

A block diagram of the experimental arrangement is shown in Fig. 1. A 1.5 m grating controlled  $CO_2$  laser is used which produces 2-4 W,  $TEM_{00}$  mode, on any one of ~ 50  $CO_2$  lines. A small 650 Hz dither is applied to the output mirror producing a variation in the discharge tube impedance. This signal is used to lock the laser to the peak of its gain curve with a long term frequency stability of ~1 MHz. The short term frequency jitter is less than 100 MHz.

The NH<sub>2</sub>D gas samples are held in a Stark cell equipped with NaCl windows and containing two  $4 \times 30$ cm long glass plates metallized on their inner surfaces and separated by  $0.5946 \pm 0.0005$  mm quartz spacers. After passing between the Stark plates, the transmitted laser beam is monitored by a Au: Ge photoconductive detector, which in combination with a preamplifier has a bandwidth of ~ 10 MHz. A pulse generator supplies step function voltage pulses across the Stark plates at a repetition rate of ~ 20 kHz, and the detector – preamp output is fed into a PAR 162 Boxcar integrator which provides signal averaging and displays the results on an X-Y recorder.

 $NH_2D$  was synthesized by simply mixing  $NH_3$  and  $D_2O$ . The H and D atoms in both  $NH_3$  and  $D_2O$  exchange rapidly among themselves, resulting in a statistical mixture of partially deuterated water and ammonia. This mixture was vacuum distilled several times holding the mixture at -78 °C and collecting the distillate at -196 °C. Since the vapor pressure of H<sub>2</sub>O is  $10^{-3}$  Torr at -78 °C, as compared to 50 Torr for NH<sub>3</sub>, all water can be removed in this manner. The purified ammonia mixture contains  $\sim 45\%$  NH<sub>2</sub>D when a NH<sub>3</sub>: D<sub>2</sub>O ratio of 1.33:1 by volume is used.

We first examined the  $(\nu, J, M_J) = (1, 4_{04}, \pm 4) \rightarrow (2, 5_{14}, \pm 5)$  NH<sub>2</sub>D transition which was Stark tuned ~2300 MHz into resonance with the P(14) CO<sub>2</sub> laser line at 10.53  $\mu$ m.<sup>11</sup> The Stark field is perpendicular to the linearly polarized optical field so that  $\Delta M_J = \pm 1$  selection rules apply. The  $\Delta M_J = \pm 4 \rightarrow \pm 3$  component need not be considered since it has an intensity which is down by a factor of 45 from the  $\pm 4 \rightarrow \pm 5$  component. Due to the <sup>14</sup>N nuclear quadrupole moment, the  $M_J = \pm 4 \rightarrow \pm 5$  component is split into hyperfine components corresponding to  $M_I$ = 0, ±1. However, since the nuclear motion is uncoupled from the molecular rotation by the high Stark field,  $\Delta M_I = 0$  selection rules apply, and all three components





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FIG. 2. Observed and calculated nutation signals for the  $(\nu_2, J, M_J) = (0_a, 4_{04}, \pm 4) \rightarrow (1_5, 5_{14}, \pm 5)$  transition in NH<sub>2</sub>D with an incident laser power of 2.18 W.

have the same intensity and Stark effect.<sup>12</sup> Thus, the transition is effectively a simple two-level system, and the theory of Sec. II applies. An experimental nutation signal using 6.6 mTorr of  $NH_2D$  and a laser power of 2.18 W (inside the cell) is shown in Fig. 2. The laser beam profile  $E_0^2(R)$  was very nearly Gaussian, with a spot radius of 1.40±0.07 mm, and was obtained by measuring the laser intensity distribution in front of and behind the Stark cell with a small scanning aperture (<0.5 mm). These profiles were averaged, and Eq. (24) numerically integrated to obtain the points shown in Fig. 2.

In using Eq. (24), one assumes a detector area large compared to the beam size. Since our detector has a  $2\times 2$  mm cross section, this was not quite true. However, Eq. (24) should be quite adequate since we are monitoring most of the beam, and, in any event, the beam profile integration does not significantly affect the nutation frequency. This last point was verified experimentally by noting that the nutation signal was insensitive, except for overall amplitude, to the detector po-



FIG. 3. Observed and calculated nutation signals for the  $(\nu_2, J, M_J) = (0_a, 4_{04}, \pm 4) \rightarrow (1_s, 5_{14}, \pm 5)$  transition in NH<sub>2</sub>D with an incident laser power of 1.13 W.

TABLE I. Hyperfine components of the  $(0_a, 4_{04}, \pm 4) \rightarrow (1_3, 5_{14}, \pm 5)$  transition in NH<sub>2</sub>D.

Component	Relative dipole matrix element	
(± 1, ± 4) -+ (± 1, ± 5)	1.00	
$(0, \pm 4) \rightarrow (0, \pm 5)$	0.98)	splitting = 3.4 MIIz
$(0, \pm 4) \rightarrow (\pm 1, \pm 4)$	0.22)	
$(\mp 1, \pm 4) \rightarrow (\mp 1, \pm 5)$	0.80)	splitting = 1.8 MHz
$(\pm 1, \pm 4) \rightarrow (0, \pm 4)$	0.60}	

sition in the beam.

The value of  $\partial E_0/\hbar$ , where  $E_0$  is now the field intensity in the center of the beam, is  $18.0 \pm 0.36$  MHz. The error limit is determined by the accuracy of the computer fit (better than 2%). The fit was very insensitive to the value chosen for  $\tau$ . This is due to the fact that nutation signals from molecules in the center of the beam and the edge of the beam have different nutation frequencies which interfere to give a shortened lifetime for the nutation signal. The best fit was obtained for a lifetime  $\tau \sim 1.2 \ \mu \text{sec.}$ 

From the value of  $\sigma E_0/\hbar$ , the dipole matrix element can be determined if  $E_0$  is known. An absolute power measurement is required for this and was done using two Coherent Radiation Model 210 thermopiles. These devices are factory calibrated with a CO<sub>2</sub> laser to  $\pm 5\%$ using a standard traceable to NBS. We had two such meters available, and they agreed to better than 4%. An average of the two was taken as the laser power. Combining this with the measured beam profile, we obtain  $E_0 = 164 \pm 9$  V/cm. Note that the power measurement is not as critical as the beam profile measurement because  $E_0$  is proportional to the square root of the power.

The value of the transition dipole matrix element obtained from the data of Fig. 2 is then  $\vartheta = 0.0349 \pm 0.0021$ D. The bulk of the error here is due to the beam profile measurement. This could readily be made more accurate in future experiments. We also measured  $\vartheta$ using a lower laser power, 1.13 W, as shown in Fig. 3. The signal here is somewhat more sensitive to  $\tau$  because the nutation frequency is lower; however, the fit is still good and yields a value of  $\vartheta = 0.0356 \pm 0.0021$  D, in excellent agreement with the high power measurement. The average of the two values is

$$\Phi = 0.0353 \pm 0.0021 \,\mathrm{D}$$
(26)

for the  $(\nu_2, J, M_J) = (0_a, 4_{04}, \pm 4) - (1_s, 5_{14}, \pm 5)$  transition.

We also made measurements of the  $M_J = \pm 4 - \pm 5$  component of the  $(\nu_2, J) = (0_a, 4_{04}) + (1_a, 5_{05})$  transition which can be Stark tuned into resonance with the P(20) CO<sub>2</sub> laser line at 10.59  $\mu$ m.<sup>11,13,14</sup> Unfortunately, this transition is not a simple two-level system because here the <sup>14</sup>N nucleus is not completely decoupled from the molecular rotation in the 5<sub>05</sub> state.<sup>14</sup> This produces a partial breakdown of the selection rules and recent high resolution Lamb dip studies we have made show that the five hyperfine components given in Table I all



FIG. 4. Optical nutation signal for the  $(\nu_2, J, M_J) = (0_a, 4_{04}, \pm 4)$  $\rightarrow (1_a, 5_{05}, \pm 5)$  transition in NH<sub>2</sub>D with an incident laser power of 3.73 W. Upper trace is the calculated nutation signal, and the lower trace is experimental.

have appreciable intensity.<sup>15</sup>

The relative dipole matrix elements shown there can be calculated exactly from the Stark and quadrupole coupling constants determined in the Lamp dip work. 15 Note that the  $(M_I, M_J) = (0, \pm 4)$  and  $(\pm 1, \pm 4)$  lower state components are each coupled to two excited state components. For these three-level systems, the simple theory discussed previously must be modified. The density matrix equations can easily be written down, but they must be solved numerically. In practice we found it more convenient to solve the well known equations for the probability amplitudes of a three-level system as these solutions require only a numerical evaluation of the roots of a cubic equation.<sup>16</sup> The elements of the density matrix can then be constructed from the probability amplitudes and the polarization found from the appropriate generalization of Eq. (12). The remainder of the calculation proceeds in the same manner as the two-level case with numerical integrations over the molecular velocity distribution and the laser beam profile.

The calculated results for both three-level systems and the  $(\pm 1, \pm 4) \rightarrow (\pm 1, \pm 5)$  two-level system (using the proper relative dipole matrix elements) were added together to give the theoretical optical nutation signal. Figure 4 shows an experimental trace with the best calculated fit below it. Both traces show destructive interference near 1.2  $\mu$ sec caused by the three-level systems. The fit here is not quite as good as for the  $(0_a, 4_{04}, 4) \rightarrow (1_s, 5_{14}, 5)$  transition, but calculations using higher and lower values of  $\mathcal{O}E_0/\hbar$  show that the fit is accurate to at least 6%. For the data of Fig. 4, we obtain  $\mathcal{O}E_0/\hbar \simeq 22.0 \pm 1.3$  MHz. Since the laser power was  $3.73 \pm 0.18$  W and the beam radius was  $1.70 \pm 0.08$  mm, the dipole matrix element is

for the  $(0_a, 4_{04}, \pm 4) \rightarrow (1_a, 5_{05}, \pm 5)$  transition.

The vibrational part of the transition dipole matrix elements given in Eqs. (26) and (27) can be extracted by calculating the rigid rotor direction cosine matrix elements. In making this separation, it is convenient to choose a space fixed axis system in which the Stark field is along the Z axis, and the optical field is polarized along the X axis. Assuming the total wavefunction can be written as a product of electronic, vibrational, and rigid rotor wavefunctions, we have

$$\mathcal{P} = \langle \psi_{\mathbf{v}\mathbf{i}\mathbf{b}} \psi_{\mathbf{rot}} | \mu_X | \psi'_{\mathbf{v}\mathbf{i}\mathbf{b}} \psi'_{\mathbf{rot}} \rangle$$
$$= \sum_{g=a,b,c} \langle \psi_{\mathbf{v}\mathbf{i}\mathbf{b}} | \mu_g | \psi'_{\mathbf{v}\mathbf{i}\mathbf{b}} \rangle \langle \psi_{\mathbf{rot}} | \phi_{Xg} | \psi'_{\mathbf{rot}} \rangle , \qquad (28)$$

as the measured dipole matrix element. Here  $\phi_{xg}$  is a direction cosine, and  $\mu_g$  is the *g*th component of the permanent dipole moment given by  $\mu = \langle \psi_{gl} | \sum_i c_i \mathbf{r}_i | \psi_{gl} \rangle$ .  $e_i$  is the charge and  $\mathbf{r}_i$  the center of mass coordinate of the *i*th electron or nucleus in the molecule. The non-vanishing direction cosine matrix elements are

These numbers were obtained using our best estimate of the ground and excited state rotational constants.<sup>17</sup> Because these matrix elements are very insensitive functions of the rotational constants, the values should be quite accurate. For example, a 15% error in the excited state asymmetry parameter  $\kappa$  produced an error of less than 0.5% in the matrix elements. We must also take into account the fact that in the Stark field the lower state is a nearly equal mixture of the 4<sub>04</sub> and 4<sub>14</sub> rotational states. When this is done, we obtain the desired vibrational matrix elements

$$\langle \nu_2 = 0_a \left| \frac{\partial \mu_a}{\partial Q} Q \right| \nu_2 = 1_a \rangle = 0. \ 112 \pm 0. \ 009 \ \mathrm{D} ,$$

$$\langle \nu_2 = 0_a \left| \frac{\partial \mu_c}{\partial Q} Q \right| \nu_2 = 1_s \rangle = 0. \ 158 \pm 0. \ 009 \ \mathrm{D} .$$

$$(30)$$

These matrix elements are written using the conventional Taylor expansion for the dipole moment  $\mu_g = \mu_g^{0}$ +  $(\partial \mu_g / \partial Q)|_{Q=0} Q + \cdots$ , where Q is the normal coordinate associated with the  $\nu_2$  motion. Notice that the  $\langle 0_a|(\partial \mu_a / \partial Q)Q|1_a \rangle$  matrix element depends on the dipole moment derivative along the a axis which is nearly perpendicular to the three fold symmetry axis of the electronic charge distribution. While the permanent dipole moment along this axis is very small, the dipole moment derivative is substantial.

There has been one previous measurement of a vibrational transition dipole matrix element in ammonia by Shimizu *et al.*, who found

$$\langle \nu_2 = 0_a | (\partial \mu_c / \partial Q) Q | \nu_2 = 1_s \rangle = 0.24 \pm 0.02 \text{ D}$$

for  ${}^{15}\rm{NH}_3$ .  ${}^{16}$  Since we found 0.158 D for the same matrix element in NH<sub>2</sub>D, it would appear that the deuterium substitution has a very large effect on the inversion motion.

#### IV. DISCUSSION

We have shown that transition dipole matrix elements can be accurately measured using optical nutation. To our knowledge, these measurements are the first determination of dipole matrix elements for an asymmetric rotor.

It is interesting to compare the error sources in our optical nutation technique with those of the steady state laser method which measures absolute absorption vs pressure. If optical nutation is used, three error sources are important: errors in the optical nutation frequency measurement, in the total laser power measurement, and in the beam profile measurement. As discussed in Sec. III, the nutation signal can be fit to within a few percent provided no other transitions overlap the Doppler width of the line being studied. Our laser power and beam profile measurements had somewhat larger errors, but these also should be reducible to ~2% by using better equipment such as a self-calibrating power meter and a micrometer controlled scanning aperture. The steady state laser method also requires a knowledge of three parameters, each of which can contribute to the error in a dipole matrix element measurement.<sup>2</sup> These are the absolute absorption of the transition, the collision-broadened linewidth, and the absolute equilibrium populations of the upper and lower states. The absolute absorption and the collision broadened linewidth are obtained simultaneously by measuring the absolute absorption as a function of pressure, generally over a range of ~ 0.1 to 50 Torr.<sup>2</sup> Such measurements can be made quite accurately in this pressure range provided one does not have trouble with overlapping lines. However, at pressures above a few Torr the linewidths are rather large and have Lorentzian tails. Thus, finding a transition at a laser frequency with no overlap problems can be difficult. Once the absorption and linewidth have been determined, the absolute population in the upper and lower states must be calculated to find O. If care is taken to make accurate pressure measurements, this calculation is often not a problem. It does require knowledge of the transition assignment, the rotation-vibration energies, the rotational and vibrational partition functions, and the isotopic composition of the sample, however, and in some cases these are not all accurately known.

As an example of the steady state method as well as a check on our results, consider the  $(0_a, 4_{04}, \pm 4)$  $-(1_a, 5_{05}, \pm 5)$  transition in NH<sub>2</sub>D. Johnston and Mellville have measured the absorption coefficient and linewidth of this transition in the collision broadened limit, so we can try to estimate @ from their data.<sup>19</sup> The first problem one finds is that, in contrast to the Doppler broadened case, the  $M_J$  components overlap so that a sizeable correction must be made to obtain the correct absorption for the  $M_J = \pm 4 - \pm 5$  component. This correction gives  $\alpha \simeq 0.028$  cm<sup>-1</sup> at 10 Torr instead of the 0.042 cm<sup>-1</sup> overall absorption they observed at that pressure. Their linewidth measurement gives 32.5 MHz/Torr. We feel this is too high, since our preliminary photon echo measurements on this transition give 28 MHz/Torr.<sup>15</sup> The greatest uncertainty in obtaining  $\vartheta$  by this method comes from the population calculation, however. It is impossible to obtain pure NH<sub>2</sub>D due to isotope exchange reactions. Johnston and Mellville analyzed one of their samples by mass spectroscopy and found  $45 \pm 10\%$  NH<sub>2</sub>D. In addition to this uncertainty, the value of the rotational partition function does not appear to be accurately known. We calculate Q = 310, but estimates vary by about 10%. <sup>13,17</sup> Putting these numbers together, we get  $\vartheta = 0.041$  D. This is in good agreement with our nutation result [see Eq. (27)] since the error here is on the order of  $\pm 0.004$  D.

At present, a major drawback of using optical nutation to measure dipole matrix elements is that transitions with a large Stark effect are required. We wish to point out that this drawback can be removed by frequency switching the laser instead of Stark switching the molecule. This would involve placing an electrooptic modulator in the laser cavity to provide frequency modulation of the laser output, 20 Voltage pulses applied to the modulator would then shift the laser frequency enabling one to perform coherent transient experiments which are exact analogs of the Stark switching experiments. We plan to begin such experiments in the near future. One complication which appears when no electric field is present is that all transitions have an  $M_J$  degeneracy. This is not serious because the relative intensity of each component is known, although it will produce a somewhat faster decay of the optical nutation signal and some additional complexity in the calculations.

In summary, we find that optical nutation can be used to measure dipole matrix elements with accuracies comparable to the steady state laser technique. The two methods should be thought of as being complimentary because they depend on completely different parameters, although, all else being equal, the steady state technique is probably the method of choice since it requires no special equipment. However, there are many situations where steady state methods will not work well, but optical nutation will. These include molecules which have dense spectra and thus overlapping lines at high pressure, isotopically substituted molecules where the isotopic composition is not accurately known, low vapor pressure materials, and hot band transitions where the level populations may be difficult to determine. In these situations optical nutation may be used to great advantage.

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