

Experimental determination of the Einstein coefficients for the $N_2(B-A)$ transition

Lawrence G. Piper, Karl W. Holtzclaw, and B. David Green
Physical Sciences Inc., Research Park, P. O. Box 3100, Andover, Massachusetts 01810

William A. M. Blumberg
Air Force Geophysics Laboratory/LSI, Hanscom Air Force Base, Massachusetts 01731

(Received 21 November 1988, accepted 3 February 1989)

We have used a branching-ratio technique to measure the relative variation in the transition-dipole moment with internuclear separation for the $N_2(B-A)$ transition. Our spectral observations cover the range from 500 to 1800 nm, and use several different detectors and excitation sources. The data from different sets are consistent in the regions of spectral overlap. Using well established values for the radiative lifetimes of $N_2(B, v' \geq 5)$ allows the relative dipole-moment function to be placed on an absolute basis. From the dipole-moment function and a set of RKR-based Franck-Condon factors which we have computed, we derive Einstein coefficients covering the range $v' = 0-12$ and $v'' = 0-20$. Our results indicate that currently accepted lifetimes for $N_2(B, v' = 0-2)$ should be revised upwards by 20% to 40%.

I. INTRODUCTION

The currently accepted experimental values for the $N_2(B-A)$ Einstein coefficients (i.e., as tabulated in Lofthus and Krupenie¹) rest upon the variation in the electronic transition moment as a function of internuclear separation determined by Shemansky and Broadfoot.² Using a branching-ratio technique and the r -centroid approximation,³ they determined the relative variation in the transition moment with internuclear separation between 1.30 and 1.55 Å. They placed this relative curve on an absolute basis by adjusting it to give a lifetime for $v' = 3$ which agreed with one they determined directly by measuring real-time fluorescence decays following excitation of N_2 by a pulsed, electron beam.

This procedure gave lifetimes for $N_2(B^3\Pi_g)$ in modest accord ($\pm 15\%$) with those derived from most,⁴⁻⁶ but not all,⁷ recent theoretical transition-moment functions for $v' \geq 5$. The theoretical lifetimes all become increasingly longer than those derived from Shemansky and Broadfoot's work, however, for the lowest vibrational levels. This discrepancy reaches 50% for $v' = 0$. Even for the higher vibrational levels, where the agreement in the total radiative lifetimes between theory and experiment is adequate, the branching ratios for radiation from a given upper vibrational level to the various lower levels differ greatly between theory and experiment.

Shemansky and Broadfoot's Einstein coefficients for the lowest vibrational levels of $N_2(B)$ result from extrapolations of their transition-moment curve well outside the region of the measurements used to establish it. This procedure is prone to systematic error. To reconcile experiment and theory we have redetermined the relative transition-moment variation as a function of internuclear separation, using a procedure similar to that used by Shemansky and Broadfoot, but with measurements extending over a much greater range, 1.15 to 1.70 Å.

The first-positive bands arise from the $N_2(B^3\Pi_g-A^3\Sigma_u^+)$ transition, and are among the most prominent in nitrogen and air discharges of various types, in

the disturbed upper atmosphere,^{8,9} and in a number of chemiluminescent reactions.¹⁰⁻¹⁴ In addition, laser oscillation has been observed from these bands.^{15,16} In order to understand excitation mechanisms of the various first-positive sources or to quantify first-positive band lasing, one must have accurate Einstein coefficients. Furthermore, a complete set of Einstein coefficients allows one to predict emissions accurately in one region of the electromagnetic spectrum based upon observations in another region, e.g., infrared radiances can be estimated from visible intensities.

II. THEORETICAL BASIS FOR MEASUREMENTS

The r -centroid approximation was first put forth by Fraser³ and has been used extensively over the last three decades to evaluate the transition-moment function of a large number of molecular systems experimentally. Although this method has been criticized, several authors have demonstrated that it is generally accurate for most molecules having only slowly varying transition-moment functions¹⁷⁻¹⁹ (hydrides and deuterides appear to be an exception).

The intensity of a molecular emission, in units of photons $\text{cm}^{-3} \text{s}^{-1}$, is given by

$$I_{v'v''} = N_{v'} A_{v'v''} \quad (1)$$

where $N_{v'}$ is the number density in the upper-state vibrational level and $A_{v'v''}$ is the Einstein coefficient,

$$A_{v'v''} = \frac{64\pi^4 \nu_{v'v''}^3}{3h} |\langle v' | R_e(r) | v'' \rangle|^2. \quad (2)$$

Here $\nu_{v'v''}$ is the transition frequency in cm^{-1} , the integral is of the wavefunctions over the electric dipole-moment operator, and the constants have their usual meanings. This matrix element usually can be separated into two parts. One part represents the overlap of the wavefunctions of the two levels with each other, and is called the Franck-Condon factor. The other is the electronic transition moment which is a function of internuclear separation.

Fraser showed that the electronic transition moment

could generally be represented adequately at discrete points by a function (usually polynomial or exponential) of the r centroid. This quantity is an average r for each ($v' \rightarrow v''$) transition and is defined as

$$\bar{r}_{v'v''} = \frac{\langle v' | r | v'' \rangle}{\langle v' | v'' \rangle}. \quad (3)$$

By measuring the relative intensities of a number of bands with a common upper vibrational level, one can map out relative values for the electronic-transition moment at various r centroids, and thereby determine the variation in the transition moment with internuclear separation. Combining Eqs. (1) and (2) and separating the dipole-moment matrix into its component parts gives

$$I_{v'v''} = \frac{64\pi^4 \nu_{v'v''}^3}{3h} N_{v'} q_{v'v''} |R_e(\bar{r}_{v'v''})|^2, \quad (4)$$

where the Franck–Condon factor is

$$q_{v'v''} = |\langle v' | v'' \rangle|^2. \quad (5)$$

The ratio of measured band intensities to the product of the Franck–Condon factor times the cube of the transition frequency for each transition then gives a set of reduced intensities which should vary one from the other in the same way that the electronic transition moment varies with internuclear separation:

$$\frac{I_{v'v''}/q_{v'v''}\nu_{v'v''}^3}{I_{v'v''}/q_{v'v''}\nu_{v'v''}^3} = \frac{|R_e(\bar{r}_{v'v''})|^2}{|R_e(\bar{r}_{v'v''})|^2}. \quad (6)$$

This technique gives only the relative transition-moment variation. The transition-moment function is made absolute by normalizing to experimental lifetime or oscillator strength data.

The sum of the Einstein coefficients from a given upper level to all accessible lower levels equals the reciprocal of the radiative lifetime of that upper vibronic level:

$$\sum_{v''} A_{v'v''} = 1/\tau_{v'}. \quad (7)$$

Knowing the radiative lifetimes of N₂(B, v) allows one to put the relative transition-moment function on an absolute basis (*vide infra*).

Oscillator-strength data can establish one Einstein coefficient from the set of relative Einstein coefficients absolutely:

$$A_{v'v''} = \frac{8\pi^2 e^2}{m_e c \lambda_{v'v''}^2} \frac{d_l}{d_u} f_{v'v''}. \quad (8)$$

In Eq. (8) m_e is the electron rest mass, e its charge in esu, c the velocity of light, $\lambda_{v'v''}$ the transition wavelength in cm, d_u and d_l the electronic degeneracies of the upper and lower states, respectively, and $f_{v'v''}$ the oscillator strength. We are unaware of reliable oscillator-strength measurements for N₂ first-positive transitions.

We have measured the intensities of a number of first-positive bands over the wavelength region between 500 and 1700 nm. This set of sequences covers the $\Delta v = 6$ through $\Delta v = -2$ sequences and samples a range of internuclear separations between about 1.15 and 1.7 Å. We have placed our relative measurements on an absolute scale using the experimental lifetimes of Eyer and Pipkin.²⁰

III. EXPERIMENTAL

The experimental procedure involved determining first-positive spectra over the appropriate spectral regions under several different sets of conditions using monochromators with photoelectric detectors. Individual band intensities, $I_{v'v''}$, for each spectrum were determined using a computerized spectral-fitting procedure (see below). This procedure greatly reduces uncertainties introduced by spectral overlap with other first-positive bands or with other nitrogen band systems.

Three different monochromator/detector combinations and three different excitation sources were used in these studies. This allowed us to make multiple determinations of the data in the regions of spectral overlap. In addition, different excitation sources emphasize the formation of different vibrational levels. This allowed matching the source to the most appropriate wavelength region.

One approach consisted of looking at the excitation of nitrogen, at pressures on the order of a few milli Torr, by a high energy electron beam of 4.5 kV and about 15 mA. The apparatus for these observations, the LABCEDE facility at the Air Force Geophysics Laboratory (AFGL), has been described in detail previously.²¹ Basically it consists of a cylindrical vacuum chamber, 1 m diameter by 3.4 m long. The electron beam enters perpendicular to the chamber axis about 1.2 m from the viewing port in one end. Gas flows through the region irradiated by the electron beam in a few milliseconds. This prohibits the buildup of beam-created species within the irradiated volume. A 0.3 m monochromator with an S-1 photomultiplier monitored fluorescence in the chamber between 570 and 1050 nm. This spectral region encompasses the $\Delta v = 4$ through $\Delta v = 0$ sequences of the nitrogen first-positive system.

The second approach, which emphasized the short-wavelength region of the spectrum, involved observing atomic nitrogen recombination in a He/N₂ discharge afterglow. This source tends to emphasize excitation of the highest levels of N₂(B), $v' = 9-12$. A 0.5 m monochromator coupled to a thermoelectrically cooled photomultiplier with a GaAs photocathode was used for these measurements. They encompassed the spectral region between 500 and 850 nm, covering principally the $\Delta v = 6$ through $\Delta v = 2$ sequences of the first-positive system.

The third approach consisted of infrared observations of a low pressure (0.1–20 Torr), low power (10–20 W) microwave-discharge lamp in nitrogen. In these studies a 0.5 m monochromator with an intrinsic Ge detector scanned the spectral region between 700 and 1700 nm. This covered the $\Delta v = 2$ through $\Delta v = -2$ sequences of the nitrogen first-positive system.

All systems were calibrated for relative spectral response using a standard quartz-halogen lamp. The lamp and its power supply were obtained from Optronic Laboratories. When set up as prescribed on the calibration sheet, the lamp irradiance is certified to have an uncertainty of $\pm 2\%$ between 500 and 1600 nm, and $\pm 4\%$ between 1600 and 2500 nm. In the latter two systems, the light from the lamp was reflected off a BaSO₄ screen before passing through the entrance slit of the monochromator. The BaSO₄ screen is a

uniform, diffuse reflector. Its reflectivity is $99\% \pm 1\%$ between 300 and 1000 nm, and declines only slightly at longer wavelengths (94% at 1700 nm).^{22,23} We did correct for the decrease in reflectivity at the longer wavelengths.

The reason for using the $BaSO_4$ screen is to ensure the monochromator optics are filled. When the monochromator views the lamp directly, only a small portion of the grating is illuminated, and the location of the lamp image on the grating becomes a sensitive function of lamp placement. Irradiating small grating imperfections could distort the response of the instrument to the radiation. Underfilling the monochromator optics also can affect the location of the lamp image on the detector element. Any nonuniformities in detector responsivity with position across the detector surface, therefore, could lead to a distorted response-function calibration. The $BaSO_4$ screen eliminates these potential difficulties.

We confirmed the response function of the latter two systems with a second quartz-halogen lamp (also from Optronic Laboratories) and with a 1250 K black body (from Infrared Associates). Relative response functions derived from all three standard sources agreed to within $\pm 5\%$. As a final crosscheck of the relative response of the latter two systems, we compared observed intensities of the O/NO air afterglow continuum with published values.²⁴⁻²⁹ Good agreement was found in the region between 400 and 650 nm,²⁴⁻²⁷ but not in the infrared.^{28,29} Apparently most published values for the relative variation of air afterglow intensity as a function of wavelength are erroneous for $\lambda > 900$ nm. Recent observations by Bradburn and Lilienfeld³⁰ over this same spectral region support our findings.

IV. FITTING PROCEDURE

Individual band intensities were calculated from vibrational level populations determined by a spectral fitting technique.³¹ We fit regions containing only one prominent transition from the level of interest, i.e., fitting single sequences. The spectral fitting code determines vibronic-level number densities within an electronic state and corrects for spectral overlap between different bands. The general procedure involves calculating synthetic spectra whose magnitudes correspond to unit population for the bands of interest. The populations of these emitters are then adjusted in a linear least-squares fitting routine to reproduce the observed spectrum.

Spectral simulation begins by calculating line positions and their relative intensities following the methods of Kovacs.³² This procedure generates a stick spectrum which is then convoluted with a triangular slit function whose full width at half-maximum equals the monochromator band pass. We confirmed the appropriateness of a triangular slit function by scanning the monochromator over the atomic-line spectrum emanating from a pen-ray lamp, and then measuring the shapes of the spectral lines.

We used the spectroscopic constants of Roux *et al.*³³ to calculate band positions and found them to agree with our observations. Synthetic spectra generated from the constants tabulated in Lofthus and Krupenie¹ could not ade-

quately reproduce the wavelengths of the higher v' levels (even after correcting for the sign error on $\omega_e y_e$ for the A state in Lofthus and Krupenie).

The distribution of rotational populations was taken to be Boltzmann. Rotational temperatures for the microwave discharge spectra were chosen to give the best match to the observed rotational contours of the bands. These rotational temperatures varied between 450 and 1000 K in accord with our observations on microwave-discharge lamps using other techniques.³⁴ The other two excitation sources produced spectra with a room temperature, 300 K, rotational distribution.

Spectral overlap is a problem in all band sequences. Generally bands from higher vibrational levels of the $\Delta v = n - 1$ sequence overlap with the lower vibrational levels in the $\Delta v = n$ sequence. This problem is particularly severe for the $\Delta v = +3, +2, +1,$ and 0 sequences. The infrared afterglow system ($B' \ ^3\Sigma_u^- - B \ ^3\Pi_g$) and several sets of atomic-nitrogen lines contaminate the microwave-discharge spectra. The infrared afterglow system also affects the atom-recombination data. In addition, overlap with $\Delta v = n - 1$ first-positive bands is particularly severe in these data due to the larger relative populations of the high v' levels. The N_2^+ Meinel bands ($A \ ^2\Pi_u - X \ ^2\Sigma_g^+$) are prominent in the electron-impact excitation spectra. Spectral constants of Roux *et al.*³⁵ and Lofthus and Krupenie¹ were used to calculate the line positions of the $B'-B$ and $A-X$ systems, respectively.

The extent of the overlap determined the fitting strategy. In instances of partial overlap, the code determined the populations of all emitting species directly. With complete overlap or overlap from more than one band system, populations of the contaminating species were estimated by fitting adjacent regions of the spectrum which afforded more reliable estimates. These populations were then used to generate a synthetic spectrum of interfering emissions in the region of interest that subsequently was subtracted from the data. Fitting the residual spectrum then determined the intensities of interest. Bands for which the relevant feature coincided with another band of comparable or greater intensity, or which were severely overlapped with a significant band for which no independent population estimate could be made, were not used in the transition-moment determination.

Figures 1 and 2 illustrate the capabilities of the spectral fitting procedure. They show successive approximations in the fitting of the $\Delta v = 0$ sequence in the data taken on LABCED. The data are displayed as the light line, the fit as the smoother, darker line. In Fig. 1 only the $v' = 0-5$ levels of $N_2(B)$ and some atomic lines were included in the fit. Large discrepancies are evident in the fit, particularly around 920 and 950 nm. These regions contain the 1, 0 and 2, 1 Meinel bands. Including the Meinel bands in the fit and estimating contributions from the 7, 8 and 6, 7 first-positive bands gives the result displayed in Fig. 2. The entire spectral region is fit excellently, lending confidence to the accuracy of the intensity determinations.

Situations involving subtraction of interfering emissions could result in systematic errors. The particular Einstein coefficients used in the estimates determined the magnitudes of

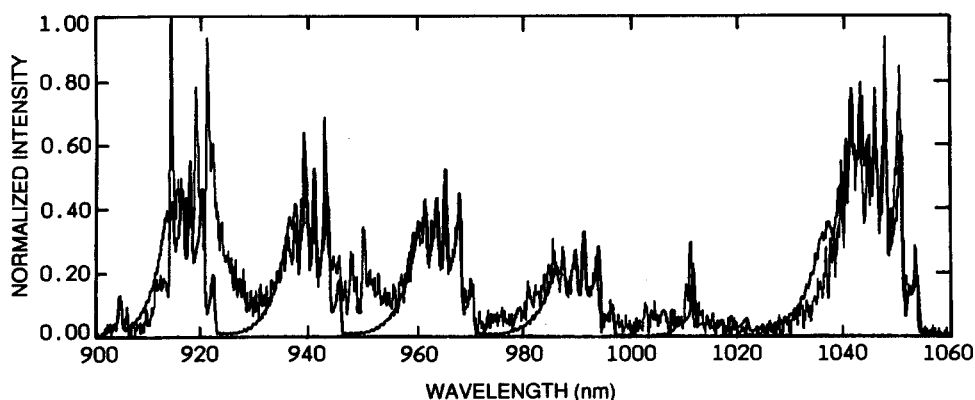


FIG. 1. $\Delta v = 0$ sequence data (light line) and fit (dark line) for $N_2(B-A)$ and atomic lines.

the intensities to be subtracted.³⁶ In regions of the spectrum where such subtraction has the potential to produce significant errors, there is overlap of data using at least two excitation methods that produce spectra with markedly different characteristics. Systematic errors would be manifest, therefore, as differing trends in the $R_e(\bar{\nu})$ curves from the different data. All systems showed similar trends, however, indicating the relatively minor role of such systematic errors.

The r centroids and Franck–Condon factors necessary for the evaluation of the reduced intensities and the construction of the $R_e(\bar{\nu})$ curve were calculated by Marinelli and Quagliaroli of PSI using a procedure outlined previously.³⁷ Rydberg–Klein–Rees potentials were first calculated for both electronic states using the spectroscopic constants of Roux *et al.*³⁵ and the approach of Tellinghuisen.³⁸ The numerical eigenfunctions were then evaluated using the Numerov–Cooley procedure³⁹ to solve the radial Schrödinger equation. The overlap integrals in the r centroid and Franck–Condon-factor calculations were evaluated using Simpson’s rule. The results, which cover the range of $v' = 0-12$ and $v'' = 0-24$, are more extensive than other calculations,^{1,35} but agree quite well with them in regions of overlap. We have tabulated them elsewhere.⁴⁰

V. RESULTS

The reduced intensities were averaged for all spectra taken with a given excitation method. A total of four spectra were analyzed for the discharge data, three for the atom-recombination data, and two for the data taken with the

LABCEDE facility. The data were combined to form the relative transition-moment curve by minimizing the sum of the squares of the differences of the normalized reduced intensities for each progression from the analytical expression which best represented all the data. In practice, we determined the best fit of a given analytical form to the reduced intensities of one progression, e.g., $v' = 2$ or $v' = 10$, and then varied the intensity normalization factor of each of the other progressions to obtain the minimum least-squares deviation from that analytical expression. We then recomputed the best-fit analytical expression to the adjusted progressions. This defined a new line, and the individual progressions were again adjusted to match this line. After several iterations, further adjustment of the progressions did not significantly improve the fit between all of the data and the analytical form which best represented them. The final result was independent of the initial progression chosen to begin the fitting procedure.

We tried both linear and quadratic expressions to represent R_e as a function of $\bar{\nu}_{v'v''}$. The fitting procedure showed the quadratic term not to be statistically significant. A few trials with a cubic function also did not improve the fit. The best linear fit was

$$R_e(\bar{\nu}_{v'v''}) = (1.670 \pm 0.043) - (0.654 \pm 0.030)\bar{\nu}_{v'v''}. \quad (9)$$

Figure 3 shows the relationship between this line and the experimental data.

The relative transition-moment curve shown in Fig. 3 was placed upon an absolute basis by multiplying Eq. (9) by a normalization factor ζ that would bring radiative lifetimes calculated from our set of Einstein coefficients into con-

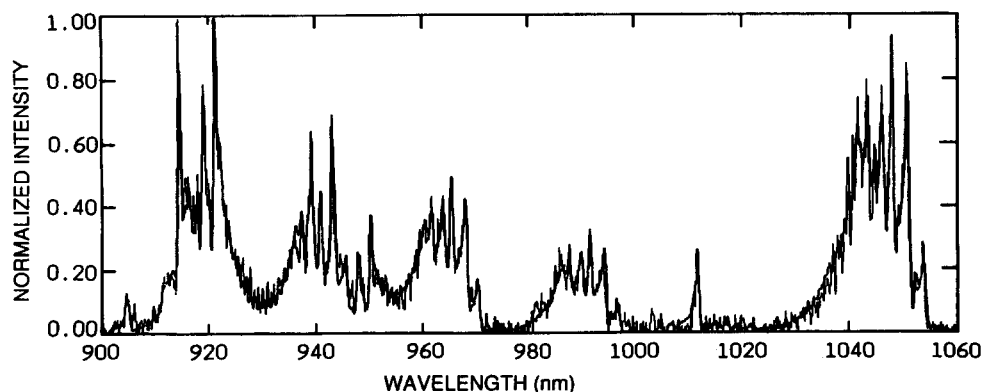


FIG. 2. $\Delta v = 0$ sequence data and fit for $N_2(B-A)$, $N_2^+(A-X)$, and atomic lines with estimated contributions from other $N_2(B-A)$ sequences subtracted.

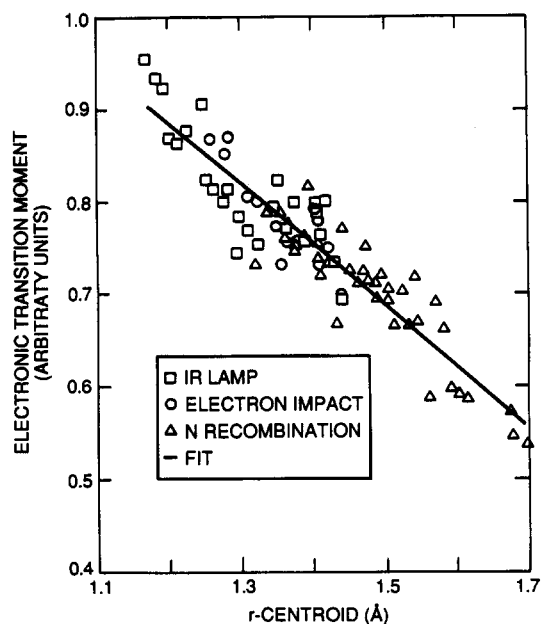


FIG. 3. Experimentally determined variation in the electronic-transition moment with r centroid for the N₂ first-positive system.

gruence with the experimental values of Eyler and Pipkin.²⁰ That is

$$\zeta \sum_{v''} q_{v'v''} \nu_{v'v''}^3 |R_e(\bar{r}_{v'v''})|_{\text{rel}}^2 = \frac{1}{\tau_{v'}} \quad (10)$$

We found a value of $\zeta = (1.89 \pm 0.03) \times 10^{-7}$ provided agreement between our calculations and all of Eyler and Pipkin's experimental lifetimes. These lifetimes, which cover the range $v' = 5$ –12, should be the most accurate available because they were determined via laser-induced fluorescence in a molecular beam under collision-free conditions. We note, however, that this set of lifetimes appear to be 10% to 15% shorter than those determined in the most reliable of the other experimental^{2,41–44} or theoretical studies.^{4–6} Our selection of a different set of lifetimes would alter our transition-moment curve by 5% to 7%. We discuss lifetimes further in Sec. VI.

The normalization factor ζ and the constants in Eq. (4) allow us to renormalize the relative transition-moment variation given by Eq. (8) so that R_e can be expressed in Debye:

$$R_e(D) = (1.298 \pm 0.040) - (0.508 \pm 0.025)\bar{r}_{v'v''} \quad (11)$$

The normalization procedure requires summing over all significant transitions. The best test for completeness is to sum the Franck–Condon factors from a given v' over all v'' . The resultant sum should be close to unity. For $v' = 0$ –10, $\sum_{v''=0}^{20} q_{v'v''} \geq 0.9$, so our set of relative Einstein coefficients is sufficiently complete for accurate normalization in Eq. (10). While the sum for $v' = 11, 12$ is somewhat smaller, our results still are sufficiently complete. Even if the Franck–Condon factor for transitions to $v'' = 21$ made up the balance of the difference between the Franck–Condon factor sum up to $v'' = 20$ and unity, the ν^3 term in Eq. (4) is so small that for these additional transitions our 21 term sum over the relative $A_{v'v''}$ would be augmented by less than 1%.

In practice a small correction to the sum in Eq. (10)

should be made to include radiative transitions to other electronic states, in this case $W^3\Delta_u$ and $B'^3\Sigma_u^-$. Werner *et al.*⁶ indicate that the largest of these corrections range from about 5% for $v' = 12$ to less than 3% for $v' = 5$. Their incorporation into our analysis will yield a normalization factor ζ which is the same within experimental error as the value we have used. We have chosen, therefore, not to make these corrections.

Table I contains a complete set of N₂(B–A) Einstein coefficients.

VI. DISCUSSION

A. Transition-moment functions

The present results agree much better with theoretical calculations^{4–6} of the transition-moment function than with the results of previous empirical investigations.^{2,45–49} In all cases agreement on the shapes is quite good over the range 1.1 to 1.7 Å. Agreement with absolute magnitudes of the transition-moment function is also quite good, generally within 10% to 15%. Our measurements appear to have resolved the major discrepancies between theory and experiment.

Figure 4 compares our experimentally derived variation in electronic transition moment with internuclear separation with that determined by Shemansky and Broadfoot² and with the theoretical calculation of Werner *et al.*⁶ The shape of our curve matches that of Werner *et al.* quite well. Consequently, our results agree quite well with theirs on the relative variation of lifetimes as a function of vibrational level and on the radiative branching ratios from a common upper vibrational level to the various lower levels. In contrast, Shemansky and Broadfoot's transition-moment function has a much different slope which results in a much different variation in lifetimes with vibrational level and set of branching ratios.

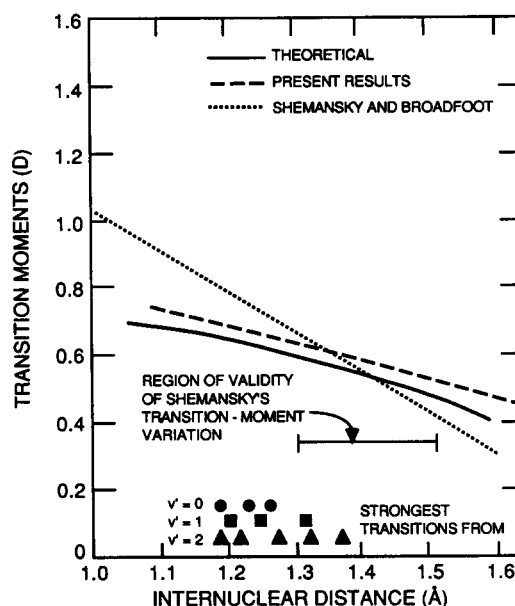


FIG. 4. Variation in electronic transition moment with internuclear distance for the N₂(B–A) transition.

TABLE I. Einstein coefficients and wavelengths for N₂ (B-A) transitions.^a

| v'/v'' | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | $\Sigma A_{v'v''}$ | v'' | $\tau_{v''}(\mu s)$ | | | | | | | | |
|----------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------------------|--------|---------------------|--------|--------|--------|--------|--------|-------|-------|------|
| 0 | 4.756 | 2.500 | 0.797 | 0.166 | 0.026 | 0.003 | 1046.9 | 1231.7 | 1489.5 | 1874.1 | 2508.6 | 3752.8 | | | | | | | | | | | 8.284 | 12.12 | | | | | | | | |
| 1 | 7.481 | 0.038 | 1.347 | 0.990 | 0.369 | 0.088 | 0.014 | 0.001 | 888.4 | 1017.9 | 1187.8 | 1420.2 | 1757.0 | 2288.4 | 3250.7 | 5521.6 | | | | | | | 10.33 | 9.68 | | | | | | | | |
| 2 | 3.962 | 5.218 | 0.964 | 0.210 | 0.747 | 0.490 | 0.178 | 0.041 | 0.005 | 773.2 | 869.6 | 990.6 | 1147.1 | 1357.2 | 1653.9 | 2104.1 | 2867.5 | 4442.9 | | | | | 11.82 | 8.46 | | | | | | | | |
| 3 | 1.024 | 7.500 | 1.901 | 2.262 | 0.059 | 0.275 | 0.429 | 0.235 | 0.077 | 0.016 | 0.002 | 685.8 | 760.6 | 851.6 | 964.8 | 1109.2 | 1299.8 | 1562.5 | 1947.5 | 2565.3 | 3717.0 | 6614.8 | 13.78 | 7.26 | | | | | | | | |
| 4 | 0.154 | 3.292 | 8.069 | 0.147 | 2.382 | 0.578 | 0.015 | 0.255 | 0.248 | 0.117 | 0.034 | 0.005 | 617.3 | 677.2 | 748.5 | 834.5 | 940.4 | 1073.9 | 1247.1 | 1480.8 | 1812.7 | 2320.8 | 3194.7 | 5047.7 | 15.30 | 6.54 | | | | | | |
| 5 | 0.017 | 0.688 | 5.842 | 6.835 | 0.232 | 1.585 | 1.162 | 0.075 | 0.074 | 0.189 | 0.137 | 0.056 | 0.014 | 0.002 | 562.2 | 611.4 | 668.9 | 736.8 | 818.1 | 917.3 | 1040.8 | 1198.7 | 1407.3 | 1695.5 | 2118.9 | 2800.8 | 4079.4 | 7339.2 | 16.91 | 5.91 | | |
| 6 | 0.001 | 0.076 | 1.579 | 8.105 | 4.479 | 1.380 | 0.610 | 1.369 | 0.368 | ... | 0.095 | 0.128 | 0.075 | 0.026 | 0.005 | 516.8 | 558.2 | 605.7 | 660.8 | 725.5 | 802.5 | 895.4 | 1009.8 | 1153.9 | 1592.4 | 1949.1 | 2492.8 | 3421.4 | 5362.5 | 18.30 | 5.46 | |
| 7 | ... | 0.003 | 0.200 | 3.060 | 9.536 | 2.180 | 2.610 | 0.059 | 1.146 | 0.691 | 0.075 | 0.019 | 0.086 | 0.079 | 0.040 | 0.012 | 0.002 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 19.80 | 5.05 |
| 8 | ... | ... | 0.013 | 0.477 | 4.655 | 9.952 | 0.582 | 3.259 | 0.094 | 0.671 | 0.861 | 0.261 | 0.004 | 0.034 | 0.066 | 0.049 | 0.022 | 0.006 | 0.001 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 21.00 | 4.76 |
| 9 | ... | ... | ... | 0.030 | 0.891 | 6.661 | 9.158 | 0.006 | 3.140 | 0.635 | 0.224 | 0.803 | 0.465 | 0.076 | 0.002 | 0.037 | 0.048 | 0.030 | 0.012 | 0.003 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 22.22 | 4.50 |
| 10 | ... | ... | ... | 0.001 | 0.072 | 1.524 | 8.506 | 7.736 | 0.340 | 2.435 | 1.335 | 0.005 | 0.554 | 0.581 | 0.206 | 0.015 | 0.009 | 0.033 | 0.033 | 0.019 | 0.007 | ... | ... | ... | ... | ... | ... | ... | ... | ... | 23.41 | 4.27 |
| 11 | ... | ... | ... | ... | 0.001 | 0.129 | 2.336 | 10.03 | 5.752 | 1.330 | 1.470 | 1.862 | 0.116 | 0.274 | 0.562 | 0.344 | 0.083 | 0.001 | 0.014 | 0.027 | 0.024 | ... | ... | ... | ... | ... | ... | ... | ... | ... | 24.35 | 4.11 |
| 12 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 25.00 | 4.00 |

^aThe order of entries is $A_{v'v''}$ in units of 10^4 s^{-1} , $\lambda_{v'v''}$ in units of nm.

Werner *et al.* have reviewed the various experimental and theoretical transition-moment functions. All of the previous empirical values⁴⁵⁻⁴⁹ diverge even more widely from our results than those of Shemansky and Broadfoot.² These discrepancies can result from a number of factors depending upon the approach taken. For example, measurements of band intensities require extreme care in determining instrument response function, in separating out contributions to the apparent band intensity from overlapping radiators, and in avoiding experimental pitfalls such as self-reversal, which apparently can be a problem using high intensity sources.⁴⁹⁻⁵¹

Accurate response-function determinations require uniformly filling the optical system with the calibration lamp output as well as with the radiation source being measured. Monochromator optics usually cannot be filled by placing a tungsten strip lamp in front of the entrance slit. Rather, illumination from the strip lamp must be reflected into the monochromator from a diffuse white source such as a $BaSO_4$ screen^{22,23} or a Spectralon[®] target.⁵²

The first-positive system is subject to significant overlap from interfering radiators. This interference is so pervasive that accounting for it requires spectral-fitting capability. Shemansky and Broadfoot did use spectral fitting in their analysis. Other groups measuring band intensities did not.

Jeunehomme⁴⁶ tried to infer a transition-moment function from lifetime measurements of various vibrational levels. Generally, radiative lifetimes cannot be determined accurately enough for this procedure to prove successful. In even the best circumstances, radiative lifetime variations with v' are fairly insensitive to the form of the transition-moment function. This is because the total radiative decay rate (the inverse of the radiative lifetime) is the sum of a number of components which, taken together, sample a wide range of internuclear separations. Comparing to experimental variations in radiative lifetime, however, provides a good cross check to a transition-moment function derived from other measurements (wide infrared).

Several groups also have attempted to measure transition moments by observing the radiation emitted by high temperature gases in thermal equilibrium.^{49,53-56} In this approach, the gas generally is heated by a shock wave or high current arc. These measurements often are plagued by interfering impurity emissions, and generally lead to overestimates of transition probabilities. Such measurements have proven to have uncertainties of factors of 2 to 3.

B. Radiative lifetimes

Figure 5 compares lifetimes calculated from the present results with those of Shemansky and Broadfoot² as well as the recent measurements of Eyler and Pipkin²⁰ and the theoretical calculations of Werner *et al.*⁶ Our transition-moment function reproduces quite well the change in lifetime with vibrational level observed by Eyler and Pipkin. The discrepancy between our results and those of Shemansky, on the other hand, is considerable. Although somewhat different in magnitude, our relative changes in lifetime with vibrational level match those calculated by Werner *et al.*

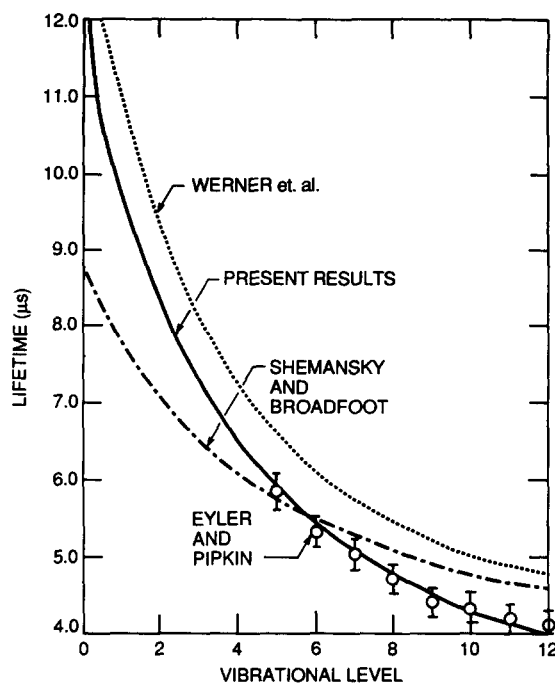


FIG. 5. Variation in $N_2(B)$ radiative lifetimes as a function of vibration level.

We scaled Werner *et al.*'s results to Eyler and Pipkin's lifetimes by first fitting their transition-moment variation to a quadratic function. This quadratic function was used as a relative R_e function to calculate relative transition probabilities. The relative probabilities were then made absolute by applying the procedure given by Eq. (10). This resulted in a 9% increase in Werner *et al.*'s transition-moment curve at every point. The result of this procedure is a set of lifetimes which agree with ours to better than 5%.

Similar treatment of the theoretical transition-moment functions of Yeager and McKoy⁴ and Weiner and Öhrn⁵ result in even smaller increases in the magnitude of their functions. Rizzo *et al.*'s⁷ function, on the other hand, requires a 12% decrease in magnitude for it to come into congruence with ours. Their transition-moment function results in a set of radiative lifetimes more than 20% shorter than those measured by Eyler and Pipkin.²⁰

A number of groups have reported experimental values for radiative lifetimes of various vibrational levels of $N_2(B)$.^{20,41-44,57,58} Table II summarizes some of them. In most instances the measurements involved fitting multiexponential decays at a number of pressures and extrapolating one of the decay components to zero pressure. This approach generally is hazardous unless the lifetimes of the various components in the decay differ greatly. The $N_2(B)$ state is collisionally coupled to various levels of the $B' \ ^3\Sigma_u^-$, $W \ ^3\Delta_u$, and $A \ ^3\Sigma_u^+$ states.^{42,44,58-63} Coupling effects are manifest even at pressures as low as a mTorr.^{42,44,63} This coupling typically leads one to overestimate the radiative lifetime. Eyler and Pipkin's measurements, having been made by laser-induced-fluorescence techniques in the collision-free environment of a molecular beam, should be free from these effects of interstate coupling.

TABLE II. N₂(B³Π_g) lifetimes in microseconds.

| <i>v'</i> | This Shemansky work (Ref. 44) | Eyler and Pipkin (Ref. 20) | Jeunehomme (Ref. 41) | Carlson <i>et al.</i> (Ref. 42) | Holstein <i>et al.</i> (Ref. 43) |
|-----------|-------------------------------|----------------------------|----------------------|---------------------------------|----------------------------------|
| 0 | 12.1 | | 8.0 | | |
| 1 | 9.7 | | 7.5 | | |
| 2 | 8.5 | 7.6 ± 0.5 | 7.0 | 8.3 ± 0.5 | 7.5 ± 0.2 |
| 3 | 7.3 | 6.6 ± 0.2 | 6.8 | 7.4 ± 0.5 | 6.6 ± 0.3 |
| 4 | 6.5 | 6.1 ± 0.2 | 6.5 | 7.0 ± 0.5 | |
| 5 | 5.9 | 5.4 ± 0.2 | 5.9 ± 0.2 | 6.2 | 6.9 ± 0.5 |
| 6 | 5.5 | 5.7 ± 0.3 | 5.3 ± 0.2 | 6.0 | 5.9 ± 0.5 |
| 7 | 5.1 | 5.3 ± 0.3 | 5.0 ± 0.2 | 5.3 | 5.7 ± 0.5 |
| 8 | 4.3 | 4.8 ± 0.2 | 4.7 ± 0.2 | 5.1 | 5.3 ± 0.5 |
| 9 | 4.5 | 5.0 ± 0.2 | 4.4 ± 0.2 | 4.8 | 5.4 ± 0.5 |
| 10 | 4.3 | 5.2 ± 0.3 | 4.3 ± 0.2 | 4.4 | 5.9 ± 0.5 |
| 11 | 4.1 | 4.7 ± 0.2 | 4.2 ± 0.2 | | 5.0 ± 0.5 |
| 12 | 4.0 | 4.5 ± 0.3 | 4.1 ± 0.2 | 4.6 ± 0.5 | 4.1 ± 0.2 |

Our results indicate lifetimes for vibrational levels 0 and 1 N₂(B), that are 36% and 24% longer, respectively, than those given by Shemansky and Broadfoot.² The discrepancy could be even greater since Shemansky and Broadfoot's values for the highest vibrational levels are 10% to 15% longer than ours. Scaling their results down accordingly would lead to discrepancies greater than 50% for *v'* = 0, 1. Ortiz *et al.*⁵⁷ and Heidner *et al.*'s⁵⁸ experimental values of 13 ± 1 μs and 10 ± 2 μs, respectively, for the radiative lifetime of *v'* = 0 appear to confirm our result of 12.1 μs.

VII. SUMMARY AND CONCLUSIONS

We have determined the variation in the transition moment with internuclear separation for the N₂(B–A) transition. Our approach relies on the redundancy of intensity measurements from several different sources using several different detection systems to reduce possible systematic errors. We have made extensive use of spectral fitting to reduce uncertainties in band-intensity determinations caused by overlap with other bands or band systems. Our results agree well with several recent theoretical calculations, but show that substantial revision of currently accepted experimental values is necessary.

Number densities of N₂(B, *v*) determined in experiments on N₂(B) excitation by various sources result from dividing measured band intensities by the appropriate Einstein coefficient. Our results indicate that using the Einstein coefficients in Lofthus and Krupenie will result in *over* estimates of 30% to 60% for the number densities in *v'* = 10–12 but *under* estimates of 20% to 30% in the lowest levels. This means that relative number densities of vibrational levels 0 and 12 could differ by 100% or more using our Einstein coefficients compared to previous values.

ACKNOWLEDGMENTS

We appreciate financial support from the Air Force Office of Scientific Research (Task 2310G4) and the Defense Nuclear Agency (Project SA, Task SA/SDI, Work Unit 00175) through contracts with the Air Force Geophysics Laboratory F19628-84-C-0057 and F19628-85-C-0032. W.

J. Marinelli and T. Quagliaroli calculated the Franck–Condon factors used to reduce the data. Experimental and analytical contributions of H. C. Murphy and M. A. DeFaccio proved invaluable as did discussions with W. J. Marinelli and W. T. Rawlins.

¹A. Lofthus and P. H. Krupenie *J. Phys. Chem. Ref. Data* **6**, 113 (1977).

²D. E. Shemansky and A. L. Broadfoot *J. Quant. Spectrosc. Radiat. Transfer* **11**, 1385 (1971).

³P. A. Fraser, *Can. J. Phys.* **32**, 515 (1954).

⁴D. L. Yeager and V. McKoy, *J. Chem. Phys.* **67**, 2473 (1977).

⁵B. Weiner and Y. Öhrn *J. Chem. Phys.* **80**, 5866 (1984).

⁶H. J. Werner, J. Kalcher, and E. A. Reinsch, *J. Chem. Phys.* **81**, 2420 (1984).

⁷A. Rizzo, R. L. Graham, and D. L. Yeager, *J. Chem. Phys.* **89**, 1533 (1988).

⁸A. Vallance Jones, *Sp. Sci. Rev.* **11**, 776 (1971).

⁹A. Vallance Jones, R. R. Meier, and N. N. Shefor, *J. Atmos. Terr. Phys.* **47**, 623 (1985).

¹⁰R. D. Kenner and E. A. Ogryzlo, in *Chemi- and Bioluminescence*, edited by J. G. Burr, (Marcel Dekker, New York, 1985), p. 45.

¹¹S. J. Davis and R. D. Coombe, *J. Phys. Chem.* **89**, 5206 (1985).

¹²S. J. Davis and L. G. Piper, *J. Phys. Chem.* (submitted, 1989).

¹³L. G. Piper, *J. Chem. Phys.* **88**, 6911 (1988).

¹⁴L. G. Piper, *J. Chem. Phys.* (in press).

¹⁵L. E. S. Mathias and J. T. Parker, *Appl. Phys. Lett.* **3**, 16 (1963).

¹⁶D. L. Franzen, B. L. Danielson, and G. W. Day, *IEEE J. Quant. Electron.* **14**, 402 (1978).

¹⁷R. W. Nicholls, *J. Quant. Spectrosc. Radiat. Transfer* **14**, 233 (1974).

¹⁸J. L. McCallum, *J. Quant. Spectrosc. Radiat. Transfer* **21**, 563 (1979).

¹⁹S. M. Yazykova and E. V. Butyraskaya, *J. Phys. B* **13**, 3361 (1980).

²⁰E. E. Eyler and F. M. Pipkin, *J. Chem. Phys.* **79**, 3654 (1983).

²¹L. G. Piper, B. D. Green, W. A. M. Blumberg, and S. J. Wolnik, *J. Chem. Phys.* **82**, 3139 (1985).

²²F. Grum and G. W. Luckey, *Appl. Opt.* **7**, 2289 (1968).

²³F. Grum and T. E. Wightman, *Appl. Opt.* **16**, 2775 (1977).

²⁴A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.* **40**, 64 (1964).

²⁵M. Sutoh, Y. Morioka, and M. Nakamura, *J. Chem. Phys.* **72**, 20 (1980).

²⁶M. Vanpee, K. D. Hill, and W. R. Kineyko, *AIAA J.* **9**, 135 (1971).

²⁷A. M. Privilov and L. G. Smirnova, *Kinet. Catal.* **19**, 202 (1978).

²⁸M. F. Golde, A. E. Roche, and F. Kaufman, *J. Chem. Phys.* **59**, 3953 (1973).

²⁹A. T. Stair, Jr. and J. P. Kennealy, *J. Chim. Phys. Chim. Biol.* **64**, 124 (1967).

³⁰G. Bradburn and H. Lilenfeld, *J. Phys. Chem.* **92**, 5266 (1988).

³¹(a) L. G. Piper, W. J. Marinelli, W. T. Rawlins, and B. D. Green, *J. Chem. Phys.* **83**, 5602 (1985); (b) M. E. Fraser, W. T. Rawlins, and S. M. Miller, *J. Chem. Phys.* **88**, 538 (1988).

³²I. Kovacs, *Rotational Structure in the Spectra of Diatomic Molecules*, Adam Hilger (London, 1969).

³³F. Roux, F. Michaud, and J. Verges, *J. Mol. Spectrosc.* **97**, 253 (1983).

³⁴(a) M. A. A. Clyne and L. G. Piper, *JCS Faraday* **72**, 2178 (1976); (b) W. T. Rawlins and L. G. Piper, *Proc. Soc. Photo-Opt. Instrum. Eng.* **279**, 58 (1981).

³⁵F. Roux, D. Cerny, and J. Verges, *J. Mol. Spectrosc.* **94**, 302 (1982).

³⁶The Einstein coefficients used in determining populations of the *v'* > 5 overlapping first positive levels (overlap of the Δ*v* = *n* and Δ*v* = *n* – 1 sequences) as well as the infrared afterglow system are those found in Ref. 6. Fitting involving the Meinel or Wu-Benes bands did not require subtraction nor did more than one band from any *v'* occur in any fit, hence the values assumed for the Einstein coefficients of those systems are immaterial.

³⁷W. J. Marinelli and L. G. Piper, *J. Quant. Spectrosc. Radiat. Transfer* **34**, 121 (1985).

³⁸J. Tellinghuisen, *Comput. Phys. Commun.* **6**, 221 (1974).

³⁹J. Eccles and R. Malik, *Quantum Chem. Prog. Exch. Bull.* **13**, 407 (1981).

⁴⁰B. D. Green, W. J. Marinelli, K. W. Holtzclaw, B. L. Upschulte, L. G. Piper, and H. C. Murphy, LABCED Final PSI TR-756 (1988). Available from the authors upon request.

- ⁴¹M. Jeunehomme, *J. Chem. Phys.* **45**, 1805 (1966).
- ⁴²T. A. Carlson, N. Duric, P. Erman, and M. Larsson, *Phys. Scripta* **19**, 25 (1979).
- ⁴³M. Holstein, D. C. Lorents, J. R. Peterson, and J. R. Sheridan, *Can. J. Chem.* **47**, 1858 (1969).
- ⁴⁴D. E. Shemansky, *J. Chem. Phys.* **64**, 565 (1976).
- ⁴⁵R. G. Turner and R. W. Nicholls, *Can. J. Phys.* **32**, 475 (1954).
- ⁴⁶M. Jeunehomme, *J. Chem. Phys.* **45**, 1805 (1966).
- ⁴⁷B. E. Cunio and R. E. W. Jansson, *J. Quant. Spectrosc. Radiat. Transfer* **8**, 1763 (1968).
- ⁴⁸(a) D. C. Jain and R. C. Sahni, *J. Quant. Spectrosc. Radiat. Transfer* **7**, 475 (1967); (b) D. C. Jain, *ibid.* **12**, 759 (1972), reanalysis of the measurements of Ref. 45.
- ⁴⁹N. E. Kuzmenko, L. A. Kuznetsova, A. P. Monyakin, and Yu. Ya. Kuznyakov, *J. Quant. Spectrosc. Radiat. Transfer* **24**, 29 (1980), and references therein.
- ⁵⁰M. E. Pillow and S. E. F. Smallwood, *Proc. Phys. Soc.* **80**, 562 (1962).
- ⁵¹D. C. Tyte, *Proc. Phys. Soc.* **80**, 1354 (1962).
- ⁵²Labsphere, Inc., N. Sutton, NH.
- ⁵³J. C. Keck, J. C. Camm, B. Kivel, and T. Wentink, Jr., *Ann. Phys.* **7**, 1 (1959).
- ⁵⁴P. A. Allen, J. C. Camm, and J. C. Keck, *J. Quant. Spectrosc. Radiat. Transfer* **1**, 269 (1961).
- ⁵⁵W. H. Wurster, *J. Quant. Spectrosc. Radiat. Transfer* **3**, 355 (1963).
- ⁵⁶K. L. Wray and T. J. Connolly, *J. Quant. Spectrosc. Radiat. Transfer* **5**, 111 (1965).
- ⁵⁷M. Ortiz, A. Perez, and J. Campos, *Physica C* **150**, 440 (1988).
- ⁵⁸R. F. Heidner, III, D. G. Sutton, and S. N. Suchard, *Chem. Phys. Lett.* **37**, 243 (1976).
- ⁵⁹N. Sadeghi and D. W. Setser, *Chem. Phys. Lett.* **77**, 304 (1981).
- ⁶⁰A. Rotem, J. Nadler, and S. Rosenwaks, *Chem. Phys. Lett.* **83**, 281 (1981).
- ⁶¹N. Sadeghi and D. W. Setser, *J. Chem. Phys.* **79**, 2710 (1983).
- ⁶²A. Rotem and S. Rosenwaks, *Opt. Eng.* **22**, 564 (1983).
- ⁶³B. D. Green, W. J. Marinelli, L. G. Piper, and W. A. M. Blumberg (manuscript in preparation).