High-Resolution Coherent Raman Spectra of Vibrationally Excited ¹⁴N₂ and ¹⁵N₂

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At an effective resolution of 0.001 cm⁻¹, we measured coherent anti-Stokes Raman spectra of electrically discharged ${}^{14}N_2$ and ${}^{15}N_2$ in the electronic ground state $X {}^{1}\Sigma_{g}^{+}$, specifically Q branches of bands with $\Delta v = 1$ up to v' = 8 for ${}^{14}N_2$ and v' = 7 for ${}^{15}N_2$, and O and S branches of the fundamental band of ${}^{15}N_2$. Account is taken of small wavenumber shifts due to pressure, AC Stark, and $|\chi|^2$ interference effects. Separate fits of the Q-branch data of each isotopic variant, combined with selected data from the literature, yield term coefficients Y_{kl} and U_{kl} or potential-energy coefficients c_j that reproduce wavenumbers of measured spectral lines generally within 0.004 cm⁻¹. The value of the harmonic vibrational parameter ω_e is 2358.5402(4) cm⁻¹ for ${}^{14}N_2$ and 2278.7913(7) cm⁻¹ for ${}^{15}N_2$. Efforts to combine spectral data of both isotopic variants to distinguish adiabatic and nonadiabatic effects arising from incomplete separation of electronic and nuclear motion in N₂ were unsuccessful. (e) 1997 Academic Press

INTRODUCTION

Although contemporary infrared spectra of polar diatomic molecular species can yield abundant measurements of wavenumbers of vibration-rotational transitions with precision typically about 0.001 cm⁻¹, or even much better $(\sim 10^{-6} \text{ cm}^{-1})$ in exceptional cases, the corresponding transition energies of nonpolar molecules are less well established. To characterize well a diatomic molecule in its ground electronic state, information about spectral parameters of many vibrationally excited states is required, but this is generally difficult to acquire. In a few cases of polar diatomic molecules that have several isotopic variants, one can deduce precise functions of potential energy and assess the importance of electronic adiabatic and nonadiabatic effects (1). An approach for acquiring analogous data for nonpolar species involves coherent Raman spectra of molecules excited in electric discharges; we present here such results for ¹⁴N₂ and ¹⁵N₂.

Previous spectral observations on ¹⁴N₂ in its electronic ground state $X {}^{1}\Sigma_{g}^{+}$ include both infrared and Raman transitions (2–9), with other information from rovibronic transitions (10). For infrared spectra, both a long cell in a laboratory (2) and the terrestrial atmosphere with the sun as source (3) enabled measurements of quadrupolar absorption of lines in the O and S branches of the fundamental band at resolutions of 0.002–0.001 cm⁻¹. Spontaneous Raman spectra were reported for the purely rotational region at a resolution of 0.1 cm⁻¹ by Butcher *et al.* (4) and at a resolution of 0.15 cm⁻¹ by Bendtsen (5), who also measured lines in the O, Q, and S branches of the fundamental vibrational band. Gilson et al. (6) measured coherent anti-Stokes Raman scattering (CARS) spectra at a resolution of 0.15 cm⁻¹ of Qbranches in the bands $1 \leftarrow 0$ and $2 \leftarrow 1$ of ${}^{14}N_2$ in a vessel at 1200 K; these measurements were not calibrated absolutely but were normalized to Bendtsen's data (5). Measurements on heated ¹⁴N₂ were made also by Lavorel and coworkers (7, 8) in the form of stimulated Raman spectra but at a resolution and absolute uncertainty of wavenumbers of about 0.002 cm⁻¹. CARS spectra with a resolution of about 0.02 cm^{-1} of ${}^{14}\text{N}_2$ in an electric discharge (9) enabled observations of vibrational states up to v = 14, and values of $\Delta G(v)$ and ΔB_v between adjacent vibrational states up to v = 11 were deduced from these experiments; wavenumbers of specific lines were not reported, and later measurements (8) from the same laboratory indicated significant deviations from these results (9).

Electronic spectra can yield information about the electronic ground state; both Edwards *et al.* (10) and Trickl *et al.* (11) deduced parameters Y_{kl} from selected data from infrared, Raman, and rovibronic spectra in global fits. Both groups rejected some Raman data; Trickl *et al.* alluded to significant inconsistencies between wavenumbers reported from diverse sources for the same transitions. The latter workers excluded measurements of spontaneous Raman scattering by Butcher *et al.* (4) and modified the CARS data of Gilson *et al.* (6) with a correction linear in wavenumber. In the same work (11) an analysis of literature data for vibrational levels $v \ge 4$ indicated the need for coefficients $Y_{k,0}$ in two sets, valid for small and large values of v. One set, consisting of three parameters, reproduces to within 0.05 cm⁻¹ the energies of states for v = 0-5, whereas the other

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FIG. 1. Diagram of the discharge cell.

set, consisting of six coefficients, produces errors <0.42 cm⁻¹ for v = 5-27.

Available spectral data of ${}^{15}N_2$ consist of purely rotational and vibration-rotational Raman transitions measured by Bendtsen (5) and CARS measurements of Q branches in the bands $1 \leftarrow 0$ and $2 \leftarrow 1$ by Gilson *et al.* (6); in both cases the resolution is 0.15 cm⁻¹ and the calibration is suspect. Hence our present knowledge of eigenenergies of N_2 in its electronic ground state and for any isotopic variant appears capable of improvement.

The objective of the present work was therefore to measure, with much improved accuracy, vibration–rotational transitions of both ¹⁴N₂ and ¹⁵N₂ to establish directly the spectral terms in the electronic ground state for v < 8. For this purpose coherent anti-Stokes Raman spectra of electrically discharged samples of both nitrogen isotopes were acquired at a resolution of 0.001 cm⁻¹. We combined our new data with complementary data selected from the literature, all suitably weighted, in order to achieve fits of wavenumbers of transitions of ¹⁴N₂ and ¹⁵N₂ to vibrational states up to v' =8 and v' = 7, respectively. Our apparatus included a novel system for recirculating a gaseous sample to make economical use of isotopic substances. These measurements and their analysis constitute this report.

EXPERIMENTAL PROCEDURE

Apparatus

To populate N_2 in excited vibrational states we subjected flowing gaseous nitrogen to an electric discharge; Fig. 1 presents a schematic diagram of the discharge cell. A power supply (Hipotronics, 25 kV and 50 mA maximum) provided a current of 7-50 mA, depending on the vibrational state, at a potential difference of 900-1000 V between tungsten electrodes 25 mm apart. The electrodes were cooled with an air stream and the temperature of the vessel's wall was less than 400 K; a minimum rate of 7 mL s⁻¹ of internal nitrogen flow was required for an optimal CARS signal. For measurements on ¹⁴N₂, gas from a commercial cylinder (99.98%) was pumped through the cell at a pressure of 4 kPa and exhausted to the atmosphere. Because ¹⁵N₂ (Matheson, 99.9% isotopic purity) is expensive, we recirculated this gas by means of a small fan (Elina, HDF4020L-12MB, dc, 4 cm, similar to those used to cool computer processor chips) enclosed in a brass chamber, as indicated in Fig. 1. In operation, the vessel was evacuated to about 3 Pa, and tested to ensure no leak; ¹⁵N₂ was admitted to the working pressure (4 kPa for Q branches and 13 kPa for O and S branches). The voltage of the fan was then adjusted to achieve rates of recirculation comparable to those in experiments on ${}^{14}N_2$, as judged from the deflection of the discharge zone and the intensity of the CARS signal.

A schematic diagram of the CARS apparatus appears in Fig. 2. The pulses (532 nm, 50 ns) from a seeded Nd-YAG laser (Continuum, custom laser, 20 Hz) were divided into five parts. Two served as pump beams (each ~15 mJ per pulse) to measure the CARS signal in a three-dimensional phase-matching arrangement (folded "BOXCARS") (12). The other three parts were employed to pump three dye cells that amplified the continuous output of a tunable ring dye laser (Coherent, CR-699-29) pumped with an Ar⁺ laser (Coherent, Innova 90, 5 W). For the purpose of calibration, a small portion of the (Stokes) output from the dye laser was used to measure absorption of I₂ vapor. The main output from the dye laser after amplification had an energy of ~1 mJ per pulse. This apparatus for measuring coherent Raman spectra has an effective resolution of about 0.001 cm⁻¹ (13).

The Stokes beam and two pump beams (532 nm) were focused with a lens (focal length 300 mm) at the downstream edge of the positive column of the glow discharge (see Fig. 1). The beam overlap, focal position, and discharge current were then adjusted for the maximum CARS signal of the branch being measured. The CARS beam so generated passed optical filters (Corning CS57 and interference with band pass at 532 nm) and a monochromator (McKee-Pedersen, MP-10118) to a photomultiplier (Hamamatsu R955). The output from this detector was integrated with a signal averager (Stanford Research, SR250), the analog output of which was digitized with a microcomputer, which served also to scan the ring dye laser in steps of 0.001 cm⁻¹.

Measurements

Representative CARS spectra obtained with the above apparatus are shown in Figs. 3 and 4, which display for ${}^{15}N_2$



FIG. 2. Schematic diagram of the high-resolution CARS apparatus.

portions of Q branches in the bands $1 \leftarrow 0$ and $7 \leftarrow 6$, respectively. The former figure illustrates the ratio of signal to noise for an undischarged sample and the latter figure shows that this ratio degrades, progressively, as the discharge current is increased to populate the higher vibrational levels. The linewidths (FWHM) typically were between 0.01 and 0.02 cm^{-1} . For the sample of Fig. 4, the intensities indicate an approximate Boltzmann distribution among rotational levels corresponding to a rotational temperature of about 700 K. In recording these spectra, 10-20 shots were averaged at each scan position and a zero level was determined before each scan on blocking the Stokes beam and averaging a few hundred laser pulses under operating conditions.

Considerable care was taken to ensure that reproducible



FIG. 3. Portion of the *Q* branch of the fundamental band of ${}^{15}N_2$.



FIG. 4. Portion of the *Q* branch of the band $7 \leftarrow 6$ of ${}^{15}N_2$.

and accurate wavenumbers of transitions were recorded. To stabilize the frequency of the Nd-YAG and Stokes lasers, we operated the entire system for 2 hr before measurements began. A reference line, $Q_0(10)$ of the fundamental band of ¹⁴N₂, was measured several times over 0.5 hr to verify that levels of jitter and drift were acceptable, such that the maximum deviation was less than 0.0012 cm^{-1} . The same line was recorded after each measurement scan of several lines of a particular Q branch of ${}^{14}N_2$, which typically took 0.5 hr, and data were accepted when the wavenumber of the reference line varied less than 0.0012 cm⁻¹. The wavenumber of line $Q_0(10)$ of ¹⁴N₂ was also adopted as an absolute standard. The mean value of this standard determined before and after measurements of other lines was set equal to the absolute value 2328.0007 cm⁻¹ from stimulated Raman spectra reported by Tabyaoui et al., who cite an uncertainty of 0.0020 cm⁻¹ (7, 8). Scans of absorption of I_2 were obtained concurrently with the measurement of the line $Q_0(10)$ and other lines, and were used to make small corrections of the latter positions relative to this standard line (see below). For measurements on ¹⁵N₂ an auxiliary standard was analogously used; a line $Q_0(7)$ of ${}^{15}N_2$ was measured 13 times with respect to the line $Q_0(10)$ of ¹⁴N₂; the result is 2251.2028 cm^{-1} and its relative accuracy is estimated to be $\pm 0.0010 \text{ cm}^{-1}$.

Precision and Accuracy

The frequency of the cw Stokes beam was measured with the wavemeter of the dye laser and used to determine the position of all measured lines relative to the standard $(Q_0(10) \text{ of } {}^{14}\text{N}_2)$. We assessed the precision and relative accuracy of this wavemeter, for which the manufacturer's specifications are reproducibility $\pm 0.00083 \text{ cm}^{-1}$ and absolute accuracy $\pm 0.0067 \text{ cm}^{-1}$. To test the precision, we measured, 10 times each, five lines of I₂ across the region of interest, in each case scanning the dye laser a few hundred cm⁻¹ to a random location before resetting it at the beginning of the scan. No adjustment was made to the dye laser or wavemeter during these measurements, and likewise for sample scans. As the mean standard error was ~0.00065 cm⁻¹ (0.0004 cm⁻¹ at best and 0.0009 cm⁻¹ at worst), the precision of the wavemeter is deemed satisfactory under these conditions.

Comparison of the measured I_2 wavenumbers with absolute values from an atlas (14) showed a small offset that, more importantly, varied by only 0.003 cm⁻¹ over the scan range 250 cm⁻¹, and in a nearly linear fashion. In practice, this small correction was redetermined for each set of lines in a measurement sequence using scans of absorption of I_2 taken concurrently with scans of N₂ of both the standard line and the lines of interest. We estimate that our accuracy relative to the $Q_0(10)$ line is better than 0.002 cm⁻¹ and that the absolute accuracy of wavenumbers reported in Tables 1 and 2 is better than 0.004 cm⁻¹, apart from the marked outliers.

Other Effects

In addition to the measurement uncertainties discussed above, several other possible sources of shifts to the Q-line positions were considered. The first of these is frequency



FIG. 5. Influence of the energy of the laser pulse on the shape of the line $Q_0(10)$ of ${}^{14}N_2$.

chirp of the cw Stokes laser due to amplification, which can produce a small shift of the order 10 MHz (15). This small effect was not measured; we assumed that it would be about the same for both the standard line $Q_0(10)$ and the other lines, so it was ignored. Also ignored was any pressure shift of the wavenumbers of the lines. Lavorel *et al.* (7) determined density coefficients that are nearly constant for Qlines in the fundamental band of ¹⁴N₂ (-0.0055 cm⁻¹/amagat) and that indicate that these shifts would be only 0.0002 cm⁻¹ at the pressures of our samples. Moreover, this shift would cancel because all Raman shifts were measured relative to $Q_0(10)$, for which the shift was corrected (8) to zero density.

A third effect considered is the AC Stark shift (*16*), which was observed for N_2 for highly intense laser beams and which is shown in Fig. 5 for the standard line for energies (total) of 20 and 40 mJ/pulse of the beam at 532 nm. Displacement of the line center was linearly proportional to the beam energy; at 30 mJ used in all measurements, the shift was about -0.0035 cm⁻¹. For a linear molecule, the AC Stark shift of a vibration–rotational level is (*16*)

$$\Delta E_{JM} = -E^2 \frac{\alpha}{4} - Ep^2 \gamma \frac{3M^2 - J(J+1)}{6(2J-1)(2J+3)}, \quad [1]$$

in which E is the amplitude of the electric field and α and γ are the spherical and anisotropic invariants of the polarizability tensor. For Q-branch transitions, the α term is the most important; to estimate whether the shift varied significantly from one Q progression to another, we used an approximate relation derived (16) for a Morse oscillator:

$$\delta \tilde{\nu}_{\rm v} / \tilde{\nu}_{\rm v}^0 = -[(3 E^2) / (16 D_{\rm e}\beta)](d\alpha/dq).$$
[2]

In this expression the left side is the ratio of the Stark shift to the unperturbed vibrational wavenumber $\tilde{\nu}_v^0$, D_e and β are conventional parameters of Morse's function for potential energy, and $d\alpha/dq$ is the derivative of polarizability α with respect to the normal coordinate q evaluated at R_e . The value of the ratio $\delta \tilde{\nu}_v / \tilde{\nu}_v^0$ from our experiment is 1.5×10^{-6} , which is reasonably consistent with the value of 5×10^{-6} from estimates of the parameters and the electric field of the laser beam at the sampling point. As this ratio is expected to be constant, the Stark shift would vary by only -0.0031 to -0.0035 cm⁻¹ over the range of our measurements. Within the stated experimental uncertainty, all Q lines, including $Q_0(10)$, experience the same Stark shift due to the optical field; hence the absolute accuracy of our measurements is unaffected by this phenomenon.

For lines in *O* and *S* branches, the situation differs. The γ term of Eq. [1] has the larger effect and some distortion of lines due to shifts in the *M* levels is expected; the effect is greatest for small *J* values and is of opposite sign for *O* and *S* branches. We estimate the shifts of the peak maxima to range from about ± 0.030 cm⁻¹ down to ± 0.003 cm⁻¹ at the average field strength of our experiment. As experimental confirmation of this effect was not made at the time of the measurement of the *O* and *S* branches the wavenumbers

of these lines listed in Table 2 are uncorrected for the AC Stark effect; for this reason they were excluded from fits to evaluate molecular parameters.

ANALYSIS OF SPECTRA

Interference Effects

To obtain accurate wavenumbers of transitions recorded in coherent anti-Stokes Raman spectra, one must take into account small interference shifts that are a consequence of the CARS signal depending on $|\chi|^2$. For an isolated spectral line the third-order electric susceptibility as a function of wavenumber is expressed (17) as

$$\chi = A_{mn} (\delta \tilde{\nu} + i \Gamma_{mn}) / (\delta \tilde{\nu}^2 + \Gamma_{mn}^2)$$
 [3]

in which $\delta \tilde{\nu} = \tilde{\nu}_{mn} - (\tilde{\nu}_1 - \tilde{\nu}_2)$. Here the symbols denote amplitude A_{mn} , wavenumber $\tilde{\nu}_{mn}$ of the transition, fixed wavenumber $\tilde{\nu}_1$ of the pump beam (from the Nd-YAG laser), tunable wavenumber $\tilde{\nu}_2$ of the Stokes beam (from the ring dye laser), and half-width Γ_{mn} of the line at half-maximum intensity. This susceptibility χ has real and imaginary parts,

$$\chi = \chi' + i\chi'', \qquad [4]$$

in which the real part

$$\chi' = A_{mn} \delta \tilde{\nu} (\delta \tilde{\nu}^2 + \Gamma_{mn}^2)$$
 [5]

has a dispersive lineshape; the imaginary part

$$\chi'' = A_{mn} \Gamma_{mn} / (\delta \tilde{\nu}^2 + \Gamma_{mn}^2)$$
 [6]

is Lorentzian and is the form observed in spontaneous and stimulated Raman spectra. For CARS, the overall shape of a line is given by the square of the susceptibility.

$$|\chi|^{2} = A_{mn}^{2} |\delta\tilde{\nu} + i\Gamma_{mn}|^{2} / (\delta\tilde{\nu}^{2} + \Gamma_{mn}^{2})^{2}$$
[7]

or

$$|\chi|^{2} = A_{mn}^{2} / (\delta \tilde{\nu}^{2} + \Gamma_{mn}^{2})$$

= $[A_{mn} \Gamma_{mn} / (\delta \tilde{\nu}^{2} + \Gamma_{mn}^{2})] [A_{mn} / \Gamma_{mn}].$ [8]

Comparing the latter expression with Eq. [6], we see that CARS and Raman lineshapes are identical:

$$|\chi|^2 = A_{mn}\chi''/\Gamma_{mn}.$$
 [9]

Hence the imaginary part of the CARS susceptibility determines the overall shape of a single isolated spectral line. The line is symmetric and the position of maximum intensity defines the wavenumber of the transition.

In the preceding discussion we assumed a negligible value for χ_{nr} , the nonresonant electronic background produced by all molecules in the sample volume, even those not in initial states resonant at $\tilde{\nu}_{mn}$. Because χ_{nr} derives mainly from the real parts of the susceptibility for the (far removed) electronic and purely rotational transitions, it is a simple constant added to the real part of the susceptibility:

$$\chi = (\chi' + \chi_{\rm nr}) + i\chi''.$$
 [10]

Thereby arises an interference term between χ' and χ_{nr} in the expression for χ^2 that produces distortion of the line from a symmetric shape: the position of maximum intensity is shifted from the formal wavenumber of the transition. Then the total susceptibility is given by

$$|\chi|^{2} = |(\chi' + \chi_{nr}) + i\chi''|^{2}$$

= $\chi^{2}_{nr} + 2\chi'\chi_{nr} + \chi'^{2} + \chi''^{2}.$ [11]

Moreover, when there are several lines in the same region of the spectrum additional interferences occur within their real and imaginary parts; the lineshape is given according to the expression

$$|\chi|^{2} = |\chi_{\rm nr} + \Sigma_{j}\chi_{j}' + i\Sigma_{j}\chi_{j}''|^{2}.$$
 [12]

To take these effects into account, we used Eq. [12] to simulate the recorded CARS spectra to derive accurate wavenumbers for the transitions. For all spectra the zero level signal, with the Stokes beam blocked, was subtracted before fitting. For each line, the fitting parameters were transition wavenumber $\tilde{\nu}_{mn}$, maximum intensity A_{mn} , and width Γ_{mn} , which was about 0.01 cm⁻¹ (0.02 cm⁻¹ for O and S lines) and due mainly to collisional broadening. A common value of the nonresonant background χ_{nr} (typically a few hundredths of the maximum A_{mn}) was used for all lines in each spectrum. The Doppler broadening was incorporated with convolution of Eq. [12] and a single Gaussian of half-width about 0.007 cm^{-1} , with increased widths used for spectra taken at increased discharge currents. The Doppler width effectively accounts also for the Gaussian instrumental halfwidth of 0.0005 cm⁻¹. The parameters were then varied in an iterative manner for a best fit according to least squares of residuals between observed and calculated wavenumbers.

An example of such a simulation for the line O(21) of $^{15}N_2$ appears in Fig. 6, which illustrates an extreme case of interference caused by χ_{nr} and the wings of the much more intense lines in the Q branch. The dispersive contribution of χ_{nr} is evident; the maximum of the line is shifted -0.0058 cm⁻¹ from the vertical line that marks $\tilde{\nu}_{mn}$ deduced in the fitting. This shift might be due partly to AC Stark distortion



FIG. 6. Displacement of the CARS peak position from the actual transition due to interference effects.

of the line, which was not taken into account in the simulation. This distortion is negligible for lines in Q branches and, as χ_{nr} is also less important, the influence of nearby transitions plays the major role in determining the interference shifts. The corrections are generally small but tend to increase for transitions at small J for which the spacing between lines is small. For example, for lines in the fundamental band of ${}^{15}N_2$ (Fig. 3), the shifts vary monotonically from -0.0015 cm⁻¹ for J = 12 to -0.0035 cm⁻¹ for J =1. The shift of the standard line $Q_0(10)$ of ${}^{14}N_2$ was -0.0012cm⁻¹; this correction is incorporated in the calculation of all relative Raman shifts.

Parameters in the Analysis of the Spectral Results

For ${}^{1}\Sigma^{+}$ or 0^{+} electronic states of a diatomic molecule containing nuclei of the same atomic number, the spectral terms are expressed (18, 19) as

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{v} + Z_{kl}^{r})$$
$$\times [v + 0.5]^{k} [J(J+1)]^{l}, \quad [13]$$

in which the parameters are functions in the reduced displacement variable $z = 2(R - R_e)/(R + R_e)$ as follows. The principal term coefficients Y_{kl} are related to the potentialenergy coefficients c_i independent of mass (19),

$$V(z) = c_0 z^2 (1 + \sum_{j=1}^{j} c_j z^j); \qquad [14]$$

the coefficients Y_{kl} consist of contributions (19)

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + \cdots$$
 [15]

of magnitude rapidly decreasing with order (as superscript); the principal contribution is composed of a factor U_{kl} , independent of mass, multiplied by the molecular reduced mass to various powers:

$$Y_{kl}^{(0)} = U_{kl}\mu^{-(k/2+1)}.$$
 [16]

The quantities Y_{kl} are the traditional coefficients, $Y_{10} = \omega_e$, $Y_{01} = B_e$, $Y_{02} = -D_e$, etc., that are deduced from fitting the wavenumbers of spectral lines.

Coefficients Z_{kl} are small terms that represent corrections arising from the approximate nature of the separation of electronic and nuclear motions according to the Born–Oppenheimer model. The auxiliary vibration–rotational coefficients Z_{kl}^{v} are functions of coefficients u_i for adiabatic effects

$$V'(z) = \sum_{j=1} m_{\rm e} u_j z^j / \mu \qquad [17]$$

and coefficients s_i for nonadiabatic vibrational effects

$$\beta(z) = \sum_{i=1} m_{\rm e} s_i z^j / \mu, \qquad [18]$$

whereas the further rotational coefficients Z_{kl}^{r} are functions of both these s_j and coefficients t_j for nonadiabatic rotational effects

$$\alpha(z) = \sum_{i=1} m_{\rm e} t_i z^j / \mu \qquad [19]$$

as explained in detail elsewhere (18, 19). Because for nonpolar diatomic molecules both atomic nuclei have the same protonic number, not only the coefficients Y_{kl} but also Z_{kl} depend on the molecular reduced mass $\mu = M_a M_b / (M_a + M_b)$, rather than Z_{kl} depending on separate reciprocal atomic masses as for heteronuclear diatomic molecules.

For nonadiabatic vibrational effects represented in $\beta(z)$, no external information is available to combine with wavenumber data in evaluating the potential-energy parameters. For polar molecules, the nonadiabatic rotational $\alpha(z)$ terms can be related to the electric dipole moment and to the rotational *g* factor, *g_J*, which is measured by means of the Zeeman effect. For several polar molecules the dipolar moment and *g* factor have been employed (*1*) in fitting wavenumber data to ensure maximal physical significance of the resulting spectral and molecular parameters. Although ¹⁴N₂ or ¹⁵N₂ lacks a permanent electric dipolar moment, a value of *g_J* is reported for ¹⁵N₂ (*20*), which we used to constrain the coefficient *t*₀ during processing of our data of ¹⁴N₂ and ¹⁵N₂ to evaluate potential-energy functions.

An alternative expression for spectral terms of empirical origin (21) is

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl} \mu^{-(k/2+1)} (1 + m_{c} \Delta_{kl} / \mu) \times [v + 0.5]^{k} [J(J+1)]^{l}, \quad [20]$$

in which the coefficients U_{kl} are already defined according to Eq. [16]. Comparison of Eqs. [13] and [20] shows that the terms containing the dimensionless parameters Δ_{kl} absorb not only adiabatic and nonadiabatic effects but also coefficients $Y_{kl}^{(2)}$ in Eq. [15]. Both expressions for E_{vl} were used in our global fits of the data for ¹⁴N₂ and ¹⁵N₂.

RESULTS

The significant results of our measurements are the wavenumbers of the vibration-rotational transitions of ${}^{14}N_2$ and ${}^{15}N_2$ that are listed in Tables 1 and 2, respectively. For ${}^{14}N_2$ we list our results for Q branches with $1 \le v'' \le 7$. In the fitting procedures we augmented these data with wavenumbers of the Q branches with v'' = 0 and 1 from Tabyaoui *et al.* (8) that include the $Q_0(10)$ standard to which all our measurements are referred and of O and S branches of the fundamental band from infrared measurements of quadrupolar absorption (3). Table 2 presents wavenumbers of our measured lines of ${}^{15}N_2$ in the Q branches of the fundamental band. Because the Stark shift was uncertain for the latter, they were excluded from the fitting calculations; instead we added the purely rotational data of Bendtsen (5) to our *Q*-branch data.

Weights of Data

Fitting data to obtain term coefficients Y_{kl} and potentialenergy parameters requires assignment of uncertainties s to serve as weights of data (as $1/s^2$) to account for variations in the accuracy of measurements with v and J and in combining data added from other sources. Our procedure involved first fitting each Q branch to a polynomial in J(J + 1) to enable us to recognize (a few) outliers, marked with * and + in Tables 1 and 2. These were then omitted to obtain, from the remaining lines, the band origins listed in the tables and a standard deviation that served as an uncertainty assigned to all lines in that branch in a subsequent global fit of all data. Printed at the bottom of each column in the tables, these uncertainties varied only slightly with the branch but increased gradually with v, reflecting the correspondingly degraded ratio of signal to noise. Outliers marked * were included in the fits but were assigned large uncertainties so as to exert a negligible effect on fitted parameters. For data used to supplement our measurements, we adopted the uncertainties specified by the original authors. Tests indicated no inconsistency among data from these sources.

Coefficients Y_{kl} and U_{kl}

The wavenumbers of ¹⁴N₂ and of ¹⁵N₂ were separately fit to selected coefficients Y_{kl} , in Eq. [13] with Z_{kl} neglected, of sufficient number to reproduce satisfactorily the lines in each set. Each model was selected on the basis of *t* tests and the maximum *F* statistic to ensure that only significant parameters were retained in this adjustment. With nine adjustable parameters the normalized standard deviations of the fits are 1.12 for ¹⁴N₂ and 1.18 for ¹⁵N₂. The derived values of Y_{kl} appear in Table 3.

For ¹⁴N₂ the coefficients of Table 3 reproduce satisfactorily the measured wavenumbers; Fig. 7 displays with square symbols our residuals (calculated - measured) for the several Q branches. In Fig. 7a, the residuals between our calculated values and the experimental measurements for v'' = 0and 1 of Tabyaoui, Gilson, and Bendtsen (and their coworkers) are shown with other symbols. As results of Tabyaoui et al. were included in the determination of parameters Y_{kl} , the residuals are small for these data, as expected, but the improved precision relative to other measurements is evident. The improvement is even greater for our calculated values versus those calculated from coefficients Y_{kl} reported by Trickl *et al.* (two sets, one for $v \le 5$ and the other for v< 27) (3) and by Lavorel *et al.* (9). Their results are shown as lines in the figures; these differences greatly exceed the scatter in our residuals.

TABLE 1Measured Wavenumbers (cm $^{-1}$) of Lines in Q Branches of $^{14}N_2$

	Q ₁ (J)	Q2(J)	Q3(J)	Q ₄ (J)	Q ₅ (J)	Q6(J)	Q ₇ (J)
origins ^a	2301.2521	2272.5574	2243.8200	2215.0479	2186.2254	2157.3625	2128.4530
J							
0	2301.2540	2272.5575	2243.8194	2215.0495			
1	2301.2186	2272,5235	2243.7845	2215.0127			
2	2301.1482	2272.4531	2243.7144	2214.9422	2186.1201	2157.2611*	
3	2301.0421	2272.3502*	2243.6089	2214.8362	2186.0169	2157.1555*	
4	2300.9004	2272.2053	2243.4700	2214.6969	2185.8700	2157.0095	
5	2300.7270	2272.0328	2243.2960	2214.5212	2185.6964	2156.8329	
6	2300.5207	2271.8219	2243.0842	2214.3059	2185.4826	2156.6179	2127.7048
7	2300.2760	2271.5755	2242.8377	2214.0614	2185.2377	2156.3696	2127.4542
8	2299.9952	2271.2962	2242.5560	2213.7798	2184.9538	2156.0861	2127.1708
9	2299.6833	2270.9828	2242.2416	2213.4638	2184.6364	2155.7684	2126.8487
10	2299.3349	2270.6321	2241.8892	2213.1098	2184.2818	2155.4154	2126.5238+
11	2298.9504	2270.2466	2241.5006*	2212.7212	2183.8944	2155.0243	2126.1027
12	2298.5320	2269.8273	2241.0860	2212.2990	2183.4702	2154.5997	2125.6720
13	2298.0794	2269.3724	2240.6300	2211.8418	2183.0153	2154.1402	
14	2297.5894	2268.8805	2240.1374	2211.3515	2182.5184	2153.6404	
15		2268.3588	2239.6127	2210.8239	2181.9900	2153.1116	
16		2267.8000	2239.0482	2210.2595	2181.4244	2152.5469	
17		2267.2028	2238.4603*	2209.6582	2180.8232	2151.9411	
18		2266.5753	2237.8284*	2209.0253		2151.3028	
19		2265.9121	2237.1624*			2150.6333	
20		2265.2115	2236.4590*			2149.9219	
21						2149.1768	
22						2148.3969	
s ^b /10 ⁻³	1.38	1.25	1.29	1.44	1.60	1.88	2.20

^a Band origins were obtained in a separate fit of each branch.

^b Standard deviation of fit of each separate branch, used for relative weighting ($w=1/s^2$) of lines in global fits. *s* values for outliers marked with * were increased by a factor of 10, values marked with + were not included in fits.

A similar plot of differences is offered for ${}^{15}N_2$ in Fig. 8, with differences deduced from the only other Raman data, from measurements of Q branches by Bendtsen (5) and by Gilson *et al.* (6). A systematic offset of about -0.05 cm^{-1} is evident for Bendtsen's Q-branch data (5); i.e., the latter wavenumbers are slightly too large. The scatter of residuals for Bendtsen's data is comparable to ours, whereas that of the data of Gilson *et al.* is much larger.

The term coefficients Y_{kl} in Table 3 are presented to a sufficient number of significant figures to calculate the transitions to 0.0001 cm⁻¹, but the statistical significance of the parameters is limited according to the standard errors listed. Comparisons with previous Y_{kl} results (3, 8, 9, 11) for ¹⁴N₂ are hindered by the variation in number of fitted parameters in the various fits; in general the major Y_{kl} values are consistent but our decreased estimated standard errors imply much increased precision. Our standard errors for Y_{kl} of ¹⁴N₂ are slightly smaller than those of ¹⁵N₂, for which no previous extensive data exist for comparison. It should be noted that, because coefficients Y_{kl} result from unconstrained fits, they

are equivalent to parameters A_{kl} discussed in Ref. (22), rather than the constrained parameters implied by Dunham's notation (23, 24). In the latter case, for example, one constraint is $-Y_{0,2} = 4Y_{0,1}^3/Y_{1,0}^2$. This distinction is minor; for ${}^{14}N_2$ and ${}^{15}N_2$ the ratio is 5.737 × 10⁻⁶ and 5.000 × 10⁻⁶ cm⁻¹, respectively, in good accord with $Y_{0,2}$ values deduced from the unconstrained fits.

To the extent that adiabatic and nonadiabatic effects and the $Y_{kl}^{(2)}$ term in Eq. [15] can be described by the Δ_{kl} coefficients, Eq. [20] enables a combined fit of ¹⁴N₂ and ¹⁵N₂ data in terms of coefficients formally independent of mass. Ten unconstrained parameters U_{kl} and two vibrational correction terms Δ_{10} and Δ_{20} were found to be statistically significant and are listed in Table 3. Compared to the two separate fits, the combined analysis decreased the number of parameters from 18 to 12, the values of which can be used for the calculation of transitions of any isotopic variant of N₂. For example, for ¹⁴N¹⁵N the parameters yield a value of 2291.34 cm⁻¹ for the ν_0 band origin of the fundamental, which is in good accord with the experimental value of 2291.33 cm⁻¹

TABLE 2 Measured Wavenumbers (cm⁻¹) of Lines in Q, S, and O Branches of ¹⁵N₂

	$O_0(J)^a$	$S_0(J)^a$	Q ₀ (J)	Q ₁ (J)	Q2(J)	Q3(J)	$Q_4(J)$	Q5(J)	$Q_6(J)$
origins ^b			2252.0802	2225.3303	2198.5441	2171.7222	2144.8605	2117.9640	2091.0316
J									
1		2270.4484	2252.0492	2225.2997	2198.5136	2171.6920		2117.9317	
2			2251.9862	2225.2372	2198.4506			2117.8684	
3	2233.4744	2285.0302	2251.8926	2225.1425	2198.3567	2171.5342	2144.6718	2117.7746	2090.8411
4			2251.7653	2225.0141	2198.2268	2171.4067	2144.5397*	2117.6438	
5	2218.4600	2299.4783	2251.6083	2224.8573	2198.0700	2171.2490	2144.3841	2117.4863	2090.5535
6			2251.4204	2224.6725	2197.8847	2171.0579	2144.1944	2117.2983	
7	2203.3206	2313.7953	2251.2015	2224.4500	2197.6654	2170.8381	2143.9752	2117.0744	2090.1376
8			2250.9502	2224.1994	2197.4113	2170.5833	2143.7211	2116.8218	
9		2327.9786	2250.6666	2223.9192	2197.1268	2170.2969	2143.4340	2116.5362	2089.5944
10			2250.3537	2223.6014	2196.8120	2169.9802	2143.1228	2116.2160	
11	2172.6957		2250.0087	2223.2567	2196,4640	2169.6335	2142.7733	2115.8676	2088.9222
12			2249.6323	2222.8792	2196.0869	2169.2523	2142.3926	2115.4820	
13	2157.2079		2249.2243	2222.4678	2195.6776	2168.8452	2141.9798	2115.0686	2088.1283
14			2248.7860	2222.0330	2195.2337	2168.4104*	2141.5350	2114.6314*	
15	2141.6095		2248.3147	2221 .5610	2194.7658	2167.9345*	2141.0584	2114.1511	2087.2003
16			2247.8114	2221.0563	2194.2609	2167.4266*	2140.5502	2113.6397	
17	2125.8955		2247.2804	2220.5220	2193.7255	2166.8923*	2140.0101	2113.0979	2086.1433
18			2246.7154	2219.9552	2193.1558	2166.3181	2139.4461	2112.5263	
19	2110.0745		2246.1217	2219.3568	2192.5592	2165.7158	2138.8417	2111.9211	2084.9647
20			2245.4931	2218.7335	2191.9308	2165.0829	2138.2058	2111.2890*	
21	2094.1443		2244.8352	2218.0708	2191.2675	2164.4219	2137.5396	2110.6191	2083.6583
22			2244.1433	2217.3792	2190.5720	2163.7213	2136.8393	2109.9159	
23			2243.4260	2216.6544	2189.8470	2162.9982	2136.1090	2109.1840	2082.2176
24			2242.6711	2215.9005	2189.0887	2162.2346		2108.4199	
25			2241.8876	2215.1144	2188.2990	2161.4428		2107.6207	2080.6501
26				2214.2941					
27				2213.4447					
s ^c / 10 ⁻³			0.96	1.61	1.69	1.73	2.11	1.88	1.76

^a Not included in fits (see text)

^b Band origins were obtained in a separate fit of each branch.

^c Standard deviation of fit of each separate branch, used for relative weighting ($w=1/s^2$) of lines in global fits. s values for outliers marked with • were increased by a factor of 10.

reported by Bendtsen (5). Overall, however, the combined fit reproduced the wavenumbers of all 356 lines of ¹⁴N₂ and ¹⁵N₂ only fairly well; the normalized standard deviation σ increased to 1.97, almost twice that of the separate fits. Addition of further U_{kl} and Δ_{kl} parameters failed to decrease σ significantly and led to large standard errors in the fitting parameters. Whether this large value of σ reflected inaccuracy of the data or inadequacy of the theoretical model was unclear; hence an alternative analysis of the mass dependence was made in terms of Eq. [13] and potential-energy coefficients c_i , defined in Eq. [14].

Potential-Energy Function

To evaluate parameters in a potential-energy function, we made fits with the program *Radiatom* (19) on data of ¹⁴N₂ and ¹⁵N₂ separately and then combined, employing the same input data sets and uncertainties specified above. The deduced parameters were R_e and coefficients c_j , $0 \le j \le 6$ (Eq. [14]); t_0 in Eq. [19] was constrained to be consistent with the magnitude of the rotational g factor, $|g_j| = 0.2593(5)$, of ¹⁵N₂ measured in experiments with molecular

beams (20), according to the relation $t_0 = g_J \mu/m_p$, in which m_p is the protonic mass; the sign of g_J was assumed to be negative (20). The fits were insensitive to the presence or absence of t_0 , but we retained this parameter in the fitting model to ensure maximal significance of other parameters. Resultant values of the parameters appear in Table 4; with eight adjustable parameters the normalized standard deviations of the separate fits are 1.17 for ¹⁴N₂ and 1.18 for ¹⁵N₂. In the combined fit, one additional parameter was found to be significant, as discussed below.

DISCUSSION

These CARS experiments at a resolution of 0.001 cm⁻¹ provide significantly improved spectral data of ¹⁴N₂ and, by means of our recirculating system, greatly extended the spectral data of ¹⁵N₂. The *Q*-branch vacuum wavenumber values of Tables 1 and 2 correspond to zero pressure and AC Stark field conditions and are believed to be accurate to ± 0.004 cm⁻¹. For the *O* and *S* lines of ¹⁵N₂, no Stark shift adjustment was made but this correction is believed to be

TABLE 3Parameters Y_{kl} and U_{kl} for ¹⁴N₂ and ¹⁵N₂^a

				¹⁴ N ₂	¹⁵ N ₂	$^{14}N_2 + ^{15}N_2$
k	1	parameter		Y_{kl}/cm^{-1}	Y_{kl}/cm^{-1}	$U_{kl}/(cm^{-1} u^{k/2+1})$
1	0	ω _e		2358.54024 ± 0.00039	2278.79126 ± 0.00072	6240.595 ± 0.019
		$\Delta_{1,0}$				$0.400 \pm 0.039^{\circ}$
2	0	$-\omega_e x_e$		-14.30577 ± 0.00026	-13.34624 ± 0.00026	-100.1121 ± 0.0096
		$\Delta_{2,0}$				5.1 ± 1.1^{b}
3	0	$\omega_e y_e$	/10 ⁻³	-5.0668 ± 0.055	-6.1977 ± 0.024	-99.8 ± 1.7
4	0	$\omega_e z_e$	/10 ⁻⁴	-1.095 ± 0.036		-44.0 ± 2.8
0	1	B_e		1.9982399 ± 0.0000045	1.865428 ± 0.000021	13.990796 ± 0.000053
1	1	$-\alpha_e$	/10 ⁻²	-1.731281 ± 0.000079	-1.564030 ± 0.00033	-32.0945 ± 0.0039
2	1	γ _e	/10 ⁻⁵	-2.8520 ± 0.018	-1.595 ± 0.082	-117.5 ± 4.3
3	1	δ_{e}	/10 ⁻⁷		-6.659 ± 0.75	-477 ± 110
0	2	$-D_e$	/10 ⁻⁶	-5.7376 ± 0.010	-5.0706 ± 0.057	-280.92 ± 0.84
1	2	$-\beta_e$	/10 ⁻⁸	-1.02171 ± 0.031	-0.969891 ± 0.40	-112.1 ± 6.7
ra	nge	;		$0 \le \mathbf{v} \le 8$	$0 \le v \le 7$	
σ				1.12	1.18	1.97

^a Coefficients Y_{kl} are quoted to a sufficient number of significant figures to reproduce experimental wavenumbers to 0.0001 cm⁻¹; coefficients U_{kl} are obtained from a combined fit of both isotopic variants; reduced masses used: for ${}^{14}N_2 \mu$ = 7.0015370037 u, for ${}^{15}N_2 \mu$ = 7.5000544865 u; uncertainties correspond to one standard deviation.

^b Coefficients Δ_{kl} have no unit; mass of electron used in their calculation is 5.485799 $\cdot 10^4$ u.

^c Normalized standard deviation.

	$^{14}N_{2}$	¹⁵ N ₂	$^{14}N_2$ and $^{15}N_2^{a}$
parameter	-	-	
c_0 / cm^{-1}	695843.57 ± 0.36	695853.0 ± 3.3	695812.7 ± 1.6
cı	-1.70398 ± 0.00011	-1.70677 ± 0.00024	-1.70461 ± 0.00015
c ₂	1.06160 ± 0.00052	1.0789 ± 0.0012	1.06512 ± 0.00073
c ₃	-0.467 ± 0.013	-0.284 ± 0.019	-0.388 ± 0.018
c ₄	0.938 ± 0.096	-0.81 ± 0.14	0.31 ± 0.13
c ₅	-0.85 ± 0.11	2.12 ± 0.16	-0.06 ± 0.14
c ₆	-9.3 ± 2.0	9.7 ± 2.7	-2.0 ± 2.7
(s ₀ or			$(1.128 \pm 0.099 \text{ or})$
$u_2/10^5 \text{ cm}^{-1}$)			7.85 ± 0.69)
t_0^{b}	-1.9307	-1.9307	-1.9307
$R_{e}/10^{-10} m$	1.0976005 ± 0.0000011	1.0976109 ± 0.0000032	1.0975992 ± 0.0000013
range	$0 \le v \le 8$	$0 \le v \le 7$	
	$0.95 \le R / 10^{-10} m \le 1.34$	$0.96 \le R / 10^{-10} m \le 1.31$	$0.96 \le R / 10^{-10} m \le 1.31$
σ	1.17	1.18	2.10

TABLE 4Parameters for ¹⁴N₂ and ¹⁵N₂

^a Parameters are obtained from the global fit of spectral data of ${}^{14}N_2$ and ${}^{15}N_2$; addition of either s_0 or u_2 , but not both, to parameters c_i and t_0 leads to equivalent fits.

^b Parameter t₀ was fixed during fitting of spectral data.

^c Normalized standard deviation. Uncertainties of parameters correspond to one standard deviation.



FIG. 7. Differences between wavenumbers of Q branches of ${}^{14}N_2$ obtained using coefficients Y_{kl} listed in Table 3 and wavenumbers from various sources. Shown with symbols are differences for experimental values from this work, from Tabyaoui *et al.* (8), from Gilson *et al.* (6), and from Bendtsen (5). Shown with lines are differences for wavenumbers calculated using coefficients Y_{kl} from Lavorel *et al.* (9) and two sets of Y_{kl} from Trickl *et al.* (11), one for $v \le 5$ and the other for v > 5. Numbers in parentheses indicate the range of J for each Q branch.

less than ± 0.030 cm⁻¹. Some confirmation of this comes from the comparison of tabulated *O* and *S* results with wavenumbers of these transitions calculated from the ¹⁵N₂ Y_{kl} parameters of Table 3; the maximum residual (calc. – obs.) for these is 0.017 cm⁻¹ for S(1) and the average difference is 0.004 cm⁻¹.



FIG. 8. Differences between calculated and experimental wavenumbers of Q branches of ${}^{15}N_2$. Calculated values are obtained using coefficients Y_{kl} listed in Table 3; experimental values are taken from this work, from Gilson *et al.* (6), and from Bendtsen (5). Numbers in parentheses indicate the range of J for each Q branch.

The adjustable c_i parameters in Table 4 define the function for adiabatic potential energy V(z) of ¹⁴N₂ and ¹⁵N₂ according to Eq. [14]. These coefficients from separate fits of data of ¹⁴N₂ and ¹⁵N₂ reproduce measured wavenumbers of transitions nearly as well as their counterparts Y_{kl} in Table 3, despite the former being one fewer in each set. Several correlation coefficients of parameters c_i have magnitudes of about 0.9; for this reason the standard errors associated with each value are only a partial measure of their significance. From the analysis, we obtain values of the adiabatic equilibrium internuclear separation $R_{\rm e}$ / 10^{-10} m = 1.097601(1) for ${}^{14}N_2$ and 1.097611(3) for ¹⁵N₂; correspondingly from c_0 , we derive values of the adiabatic vibrational force coefficient $k_e/N m^{-1} =$ 2294.722(2) for ${}^{14}N_2$ and 2294.710(3) for ${}^{15}N_2$. Although the values of coefficients $c_3 - c_6$ for ${}^{14}N_2$ and ${}^{15}N_2$ appear disparate, the corresponding potential-energy curves are nearly indistinguishable. Figure 9 displays the curve of $^{14}N_2$ within the range of energy up to the state v = 8, the highest level to which our measurements pertain. Plotted below the curve is the difference V(z) of ${}^{14}N_2 - V(z)$ of ${}^{15}N_2$, the magnitude of which is less than 3 cm⁻¹ over most of the range of validity, $0.96 \le R/10^{-10}$ m ≤ 1.31 . Because such differences divided by the vibrational energy are of the order of the ratio of electronic to nuclear mass for ¹⁴N₂, they have a magnitude expected for adiabatic effects (21); thus it might be expected that one could fit well the combined data of ${}^{14}N_2$ and ${}^{15}N_2$ with V'(z) containing coefficients u_i .

Such a result proved not to be the case. Fits of the combined spectral data to coefficients c_i plus various adjustable u_i , t_i , and s_i in Eq. [17] – [19] showed that, except with unacceptably large magnitudes of the latter parameters, the normalized standard deviation σ of such attempted fits remained greater than 2, in contrast with reduced standard deviations of about 1.2 for the separate isotopic variants. The exception was the addition of either the coefficient s_0 for nonadiabatic vibrational effects (Eq. [18]) or the coefficient u_2 for adiabatic vibrational effects (Eq. [17]). Either parameter converged to a stable and reasonable value with essentially identical values for the set of coefficients c_i , but σ was 2.10 in each case. A slight preference for s_0 over u_2 might be had from previous work on other polar molecules (1), in which terms s_i are generally more important than coefficients u_i . However, in view of the generally unsatisfactory overall fit it seems unwise to attach much meaning to the parameters s_0 and u_2 ; we conclude that the model represented by Eq. [13] is unable to fit the data to the extent achieved in these other studies, where σ was near unity (1).

The possibility that there might be a wavenumber error in the ${}^{15}N_2$ reference line relative to that of ${}^{14}N_2$ was tested by adding a shift parameter δ in the fitting process: δ was found to be negligible and no reduction in σ resulted. Similarly, multiplication with a scaling parameter linear in wavenumber gave essentially a unit value and no improvement. Our conclusion is thus that no such systematic errors exist in our data and that, even at our measurement



FIG. 9. Potential-energy curve for dinitrogen. Energies of vibrational levels are shown as horizontal solid $({}^{14}N_2)$ and dashed $({}^{15}N_2)$ lines. The dotted line represents the difference between adiabatic potential energies of ${}^{14}N_2$ and ${}^{15}N_2$.

accuracy of 0.004 cm^{-1} , random errors preclude evaluation of the small adiabatic–nonadiabatic effects in N₂.

SUMMARY

At an effective resolution of 0.001 cm⁻¹, we measured Raman spectra of ¹⁴N₂ and ¹⁵N₂ that yield improved vibration-rotational terms of states up to v = 8 of ¹⁴N₂ and v =7 of ¹⁵N₂ excited in electrical discharges. These terms of each isotopic variant are compactly represented in terms of either nine fitting coefficients Y_{kl} in Table 3 or eight fitted parameters of adiabatic potential-energy functions plus one constrained value from the rotational g factor in Table 4. Parameters in either set satisfactorily reproduce wavenumbers of transitions in Q branches of the specified bands in our data sets, generally well within the estimated absolute uncertainties of the measurement.

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