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Theoretical study of the effects of vibrational-rotational interactions on the Raman spectrum of N_2

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A systematic study of the polarizability and polarizability derivatives of N_2 is undertaken as a function of basis set and level of correlation treatment. The value obtained for the ratio of derivatives $(r_e \beta'_e / \beta_e)$ of the polarizability anisotropy $\beta = \alpha_{\parallel} - \alpha_{\perp}$ is 3.15 ± 0.2 , which is larger than the two experimental estimates of 2.63 ± 0.29 and 2.22 ± 0.44 .

I. INTRODUCTION

Polarizability anisotropies $\beta_e = (\alpha_{\parallel} - \alpha_{\perp})$ at r_e and their derivatives $\beta'_e = (\partial \beta / \partial r)$ at r_e determine both the absolute and relative intensities of vibrational and rotational Raman transitions. The magnitude of the parameter $\gamma = r_e \beta'_e / \beta_e$ determines the degree to which the intensities of vibrational-rotational Raman transitions are modified by vibrational-rotational interactions. The magnitude of these corrections affect temperature measurements^{1,2} using techniques such as rotational coherent anti-Stokes Raman spectroscopy (CARS).³

The magnitude of γ has been determined experimentally^{4,5} for N_2 from vibrational-rotational transitions in the Stokes Raman spectrum by measuring relative *O* and *S* branch intensities having the same initial rotational level. Both experiments were carried out at room temperature, and relative *S* and *O* branch intensities were observed for selected *J* values up to *J* = 14. Since the effects are proportional to B_e / ω_e , which for N_2 is quite small ($\sim 8.5 \times 10^{-4}$), considerable imprecision exists in the experimental measurements. From a least-squares analysis of the data, which incorporates the frequency-dependent response of the spectrometer, the experimental determinations gave $\gamma = 2.22 \pm 0.44$ ⁴ and $\gamma = 2.63 \pm 0.29$.⁵

There has been considerable theoretical effort⁶⁻¹³ to determine both the polarizability and polarizability derivatives of N_2 . Correlation contributions reduce both β and β' so that the parameter γ is rather insensitive to electron correlation. Hence, calculations at both the Hartree-Fock (HF) and correlated levels have produced $\gamma > 3$, which is larger than the experimental values. Also, Oddershede and Svendsen,¹³ using the second-order polarization propagator approximation (SOPPA) have shown that γ has a rather weak dependency on the frequency of the exciting light. It is this discrepancy between theory and experiment that has suggested⁵ that further detailed study, both experimental and theoretical is necessary. This work presents a systematic theoretical study of γ in the static limit.

In our study of γ we have employed contracted Cartesian Gaussian (GTO) basis sets for nitrogen varying in quality from $[5s\ 3p\ 2d]$ to $[6s\ 4p\ 3d\ 1f]$. Correlation contributions

have been considered from the complete active space self-consistent field (CASSCF) level to the multireference singles and doubles configuration-interaction level MRCI(SD). It is shown that MCSCF-type wave functions tend to systematically underestimate both β and β' , by reducing the spatial extent of the valence orbitals in the process of producing optimum correlating orbitals. This defect is corrected if the MCSCF procedure is followed by a CI(SD) calculation.

Using the $[5s\ 3p\ 2d]$ GTO basis, we have computed the polarizability anisotropy at the CASSCF and six-term reference CI(SD) level. These results are used in conjunction with the $X^1\Sigma_g^+$ RKR potential¹⁴ to determine relative intensities of the *O*, *Q*, and *S* branches as a function of *J* in the $1-0$ vibrational band. Finally, we have constructed the $1-0$ vibrational-rotational Raman spectrum with and without the effects of centrifugal distortion to demonstrate the magnitude of these corrections at room temperature.

II. METHODS

Two requirements must be met before a quantitative theoretical prediction of polarizabilities can be made: (1) a carefully chosen basis set spanning the polarization space adequately; and (2) a reliable calculation of correlation corrections. Various methods^{9,11,15-17} have been devised for the choice of the orbital exponents of the more diffuse functions needed to describe the distortion effects of the external field. Perhaps the simplest approach is selection based on continuing the approximately geometric series in the energy optimized basis to the next smaller value.⁹ Alternatively, Amos¹¹ chose his diffuse functions for N_2 by minimizing the HF energy of the molecule in the presence of a weak electric field. In our work we have used the so-called field-induced polarization functions,^{17,18} which have provided an economical description of the polarization space for a variety of molecules. However, all three approaches result in a similar choice of exponents.

The energy of a homonuclear diatomic molecule in a uniform static electric field *F* can be written in a power series

$$E(\mathbf{F}) = E(0) + \frac{1}{2} \mathbf{F} \cdot \boldsymbol{\alpha} \cdot \mathbf{F} + \dots \quad (1)$$

In the finite-field procedure employed herein, the polarizability tensor $\boldsymbol{\alpha}$ is determined by numerical differentiation of the field-dependent energy with respect to the field strength

$$\alpha_{ii} = \frac{2[E(F_i) - E(0)]}{F_i^2} \quad (2)$$

A small field of 0.005 a.u. is used so that the hyperpolarizability contributions, the first term neglected in Eq. (1), will be negligibly small. Also in cases where the Hellman-Feynman theorem is not satisfied, e.g., for CI(SD) wave functions, the polarizability components are determined from Eq. (2) as opposed to computing them from the induced dipole moments.¹⁹

For a diatomic molecule there are only two distinct nonzero elements of the polarizability tensor, the parallel polarizability $\alpha_{||} = \alpha_{xx}$ and the perpendicular polarizability $\alpha_{\perp} = \alpha_{yy} = \alpha_{zz}$. However, the two experimental observables are the spherically averaged dipole polarizability

$$\bar{\alpha} = \frac{1}{3} (\alpha_{||} + 2\alpha_{\perp}) \quad (3)$$

and the polarizability anisotropy

$$\beta = \alpha_{||} - \alpha_{\perp} \quad (4)$$

We also define the parameter

$$\gamma = r_e \beta'_e / \beta_e \quad (5)$$

where β'_e is the derivative of β at $r_e = 2.07432$ bohr.

In a vibrational-rotational Raman experiment, if the incident light is polarized perpendicular to the scattering plane and the outgoing light parallel to this plane, the intensity in the S, Q, and O branches is determined solely by the polarizability anisotropy β . For this case, the intensities of the three branches can be written^{12,20}

$$I^S = I_0 (2\pi)^4 (\bar{\nu}_0 - \bar{\nu}_{vJ}^{v'J+2})^4 N_{vJ} g_J \times \frac{(J+1)(J+2)}{10(2J+1)(2J+3)} |\langle \psi_{vJ} | \beta | \psi_{v'J+2} \rangle|^2, \quad (6)$$

$$I^Q = I_0 (2\pi)^4 (\bar{\nu}_0 - \bar{\nu}_{vJ}^{v'J})^4 N_{vJ} g_J \times \frac{J(J+1)}{15(2J-1)(2J+3)} |\langle \psi_{vJ} | \beta | \psi_{v'J} \rangle|^2, \quad (7)$$

and

$$I^O = I_0 (2\pi)^4 (\bar{\nu}_0 - \bar{\nu}_{vJ}^{v'J-2})^4 N_{vJ} g_J \times \frac{J(J-1)}{10(2J+1)(2J-1)} |\langle \psi_{vJ} | \beta | \psi_{v'J-2} \rangle|^2, \quad (8)$$

where

$$N_{vJ} = N_v \frac{(2J+1) \exp[-E(J)hc/kT]}{Q_R} \quad (9)$$

is the number of molecules in the initial state, Q_R being the rotational partition function. The nuclear statistical weight g_J for ¹⁴N₂ is six for even J values and three for odd J values. If in Eqs. (6)–(8) the matrix elements $\langle \psi_{vJ} | \beta | \psi_{v'J} \rangle$ were independent of J , the relative intensity in each branch would be determined solely by the Honl-London factors, the Boltzmann factors (tempera-

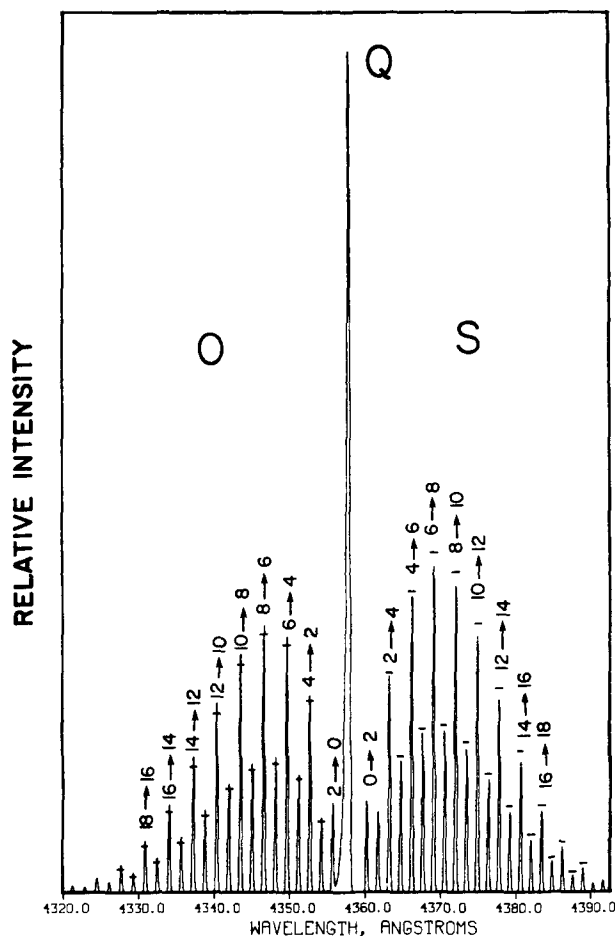


FIG. 1. The relative intensities of the O, Q, and S branches in the N₂ 1-0 vibrational-rotational Raman spectrum at 300 K. The spectrum was generated under optically thin conditions assuming excitation by 4358 Å radiation, and corresponds to a resolution of about 0.25 Å. The relative intensities calculated by assuming that the polarizability anisotropy matrix elements are independent of rotation are shown by horizontal bars. The differences are due to vibrational-rotational interactions.

ture), and the frequency differences (exciting laser frequency). At least at low temperatures, the S branch intensity is greater than the O branch because of more favorable Boltzmann factors. However, centrifugal distortion effects increase the O branch intensity relative to the S branch intensity in N₂ since $\gamma > 0$.²¹

In a typical experiment,^{4,5} one observes the ratio of the $S(J)$ and $O(J)$ intensities originating from the same J level. In this case the Boltzmann and nuclear degeneracy factors cancel and the ratio can be written as

$$\frac{I^S}{I^O} = \left(\frac{\bar{\nu}_0 - \bar{\nu}_{0J}^{1J+2}}{\bar{\nu}_0 - \bar{\nu}_{0J}^{1J-2}} \right)^4 \frac{(J+1)(J+2)(2J-1)}{J(J-1)(2J+3)} \frac{f(J)_{01}^S}{f(J)_{01}^O}, \quad (10)$$

where f is a correction factor for vibrational-rotational interaction analogous to the Herman-Wallis factor²² in the infrared. James and Klemperer²³ have derived analytical expressions for these correction factors in terms of the equilibrium rotational constant B_e and vibrational frequency ω_e assuming a harmonic oscillator approximation. To order $(B_e/\omega_e)^2$, the ratio in Eq. (10) can be written as

TABLE I. Basis set effects on the polarizability parameters of N₂.^a

	Basis set ^b				Expt. ^c
	[5s3p2d]	[6s4p2d]	[6s4p3d]	[6s4p3d1f]	
$\alpha_{ }$	14.868	14.855	14.792	14.718	15.05, ^d 14.78 ^e
α_{\perp}	10.196	10.268	10.117	10.065	10.35, ^d 10.26 ^e
$\bar{\alpha}$	11.753	11.797	11.675	11.616	11.92, ^d 11.74 ^e
β	4.672	4.587	4.675	4.654	4.66, ^f 4.70, ^d 4.45 ^e
$\bar{\alpha}'$	6.180	5.939	5.985	5.956	5.7, ^g 6.25, ^h 5.93 ⁱ
β'	6.960	7.160	7.024	7.056	8.2, ^h 6.7 ⁱ
γ	3.090	3.238	3.116	3.145	2.63 ± 0.29 ^j 2.22 ± 0.44 ^f

^aTheoretical results at the CI(SDQ) level including an estimate for the effect of unlinked clusters.(Ref. 27). All calculations were carried out at the experimental equilibrium separation of 2.07432 bohr.

^bSee the text for further definition of basis sets.

^cA correction for vibrational effects included when appropriate.

^dReference 29.

^eReference 30.

^fReference 4.

^gReference 31.

^hReference 32.

ⁱReference 33.

^jReference 5.

$$\frac{f(J)_{01}^S}{f(J)_{01}^0} = \frac{\{\gamma[1 - 3(B_e/\omega_e)^2 J(J+1)] - 4(B_e/\omega_e)(2J+3)\}^2}{\{\gamma[1 - 3(B_e/\omega_e)^2 J(J+1)] + 4(B_e/\omega_e)(2J-1)\}^2}. \quad (11)$$

Hence, the magnitude of the centrifugal distortion is inversely proportional to γ . For N₂, Svendsen and Oddershede¹² have shown that Eq. (10) is a good approximation to the correct numerical result even when the $(B_e/\omega_e)^2$ term is neglected.

Although the analytical formula [Eq. (10)] works quite well, we have computed the polarizability anisotropy β as a function of r and, using a spline representation of the data, computed the matrix elements $\langle \psi_{v,J} | \beta | \psi_{v',J'} \rangle$ numerically using the available RKR potentials.¹⁴ Even though the ratio B_e/ω_e is small for N₂, about 8.5×10^{-4} , the effects of centrifugal distortion can be clearly seen in the change in the intensity of the O lines relative to the S lines for the 1-0 vibrational-rotational Raman spectra at 300 K (see Fig. 1).

III. RESULTS AND DISCUSSION

A quantitative description of the polarizability requires a one-particle basis set containing sufficiently diffuse functions to describe the distortion of the molecule in a uniform static electric field. We began our basis set study with a [5s3p2d] GTO basis (denoted I) that consisted of Huzinaga's 9s5p set²⁴ contracted by Dunning²⁵ to [4s2p] and augmented by field-induced 1s1p2d polarization functions. The orbital exponents of the diffuse functions are $\alpha_s(0.03882)$, $\alpha_p(0.04427)$, $\alpha_d(0.1101)$, and $\alpha_d'(0.2639)$. A comparable basis set for a water molecule¹⁷ gave an average polarizability within 3% of experiment. The second basis set (II) considered was a [6s4p2d] GTO basis that contained the same 1s1p2d field-induced polarization functions as I, but

now contained the 11s7p basis of Salez and Veillard²⁶ contracted to [5s3p] according to No. 4 of their Table III and No. 5 of their Table VIII. The third basis (III) considered [6s4p3d] was basis set II augmented by a tighter d function ($\alpha_d = 0.95$). Finally, we considered a [6s4p3d1f] basis, which is basis set III augmented by $\alpha_f = 1.0$.

The results of our basis set study are summarized in Table I. All calculations include all single and double excitations from the HF reference (1s frozen) plus an estimate of the energy contribution from unlinked clusters.²⁷ The derivatives were obtained from calculations at R_e and $R_e \pm 0.1$ bohr. Trial calculations at $R_e \pm 0.025$ bohr gave nearly identical results. All calculations were done with the MOLECULE-SWEDEN program set.²⁸ Various experimental estimates²⁹⁻³³ of the polarizability parameters are also included in Table I. Where appropriate, these values include an approximate vibrational correction from $v=0$ to r_e by

$$P_0 = P_e + \frac{3B_e r_e}{2\omega_e} \left(1 + \frac{\alpha_e \omega_e}{6B_e^2} \right) (\partial P / \partial r)_{r_e} \quad (12)$$

using the experimental spectroscopic constants. However, it should be emphasized that all of the theoretical values were computed in the static limit, whereas the experimental values were determined at finite wavelengths. From the SOPPA results of Oddershede and Svendsen,¹³ one can see that all the parameters $\bar{\alpha}$, β , $\bar{\alpha}'$, β' , and γ increase slightly as the wavelength of the exciting laser light decreases. From Table I one can see that the [5s3p2d] basis gives an adequate description of the polarizability parameters, and that further augmentation of the basis to [6s4p3d1f] does not have a dramatic effect. Also, except for the two recent deter-

TABLE II. Correlation effects on the polarizability and polarizability derivatives of N₂.^a

	Method				
	SCF	CASSCF ^b	CI(SD) ^c	CI(SDQ) ^d	MRCI(SD) ^e
$\alpha_{ }$	14.908	13.542	14.782	14.868	14.758
α_{\perp}	9.514	9.472	10.011	10.196	10.190
$\bar{\alpha}$	11.312	10.829	11.602	11.753	11.713
β	5.394	4.070	4.771	4.672	4.569
$\bar{\alpha}'$	7.194	5.748	6.240	6.180	5.981
β'	7.960	5.880	7.152	6.960	7.023
γ	3.061	2.997	3.110	3.090	3.188

^aAll calculations carried out with a [5s3p2d] Gaussian basis at $r_e = 2.07432$ bohr.

^bThe active space consisted of the nitrogen 2p electrons.

^cAll single and double excitations from the HF reference (1s frozen).

^dIncludes an estimate for the effect of unlinked clusters (Ref. 27).

^eAll single and double excitations from the six most important reference configurations in the CASSCF wave function.

minations^{4,5} of the parameter γ , the theoretical values are in excellent accord with experiment. It should be noted that the two determinations^{32,33} of β' , based on measurements of the differential cross section and depolarization ratio, although not very accurate, support the theoretical values of γ .

Since the [5s 3p 2d] GTO basis provides an adequate description of the polarizability parameters, we used this basis in our study of the importance of electron correlation. The results of our study are summarized in Table II. At the HF level, the parameters β , β' , and $\bar{\alpha}'$ are all substantially overestimated. When the calculations are extended to the CASSCF level, in which the nitrogen 2p electrons are active and the 1s and 2s electrons are inactive, the magnitude of all three parameters decreases dramatically. At the CI(SD) level from the HF reference, these parameters are intermediate between the HF and CASSCF results, and in much better agreement with the experimental values²⁹⁻³³ (see Table I). The parameters were further slightly modified by a correction for the effect of unlinked clusters²⁷ CI(SDQ). Finally, we ran a multireference singles and doubles calculation using the natural orbitals from the CASSCF wave function. The reference list included six spatial occupancies (seven configuration state functions), and accounted for about 99% of the CASSCF wave function at r_e . This calculation gave parameters in good agreement with the CI(SDQ) results.

It is apparent from Table II that all of the CASSCF polarizability parameters are systematically too small. This results from the reduction in the spatial extent of the MCSCF wave function during the process of obtaining good correlating orbitals. At r_e , the expectation values of r^2 at the SCF, CASSCF, and CI(SD) levels are 24.42, 24.12, and 24.63 a.u., respectively. Hence, it is imperative to follow any MCSCF procedure

[including limited MCSCF calculations such as generalized valence bond (GVB)] by a single and double excitation CI treatment in order to properly span the polarization space.

The results of the present theoretical study are compared with previous theoretical results in Table III. The results of Morrison and Hay⁷ using GVB wave functions and the results of Kendrick¹⁰ using the method of antisymmetrized product of strongly orthogonal geminals (APSG) are qualitatively similar to our CASSCF results. Again, the orbital optimization process reduces the spatial extent of the orbitals and therefore the magnitude of the polarizability, whereas the true effect of electron correlation is to slightly increase the total polarizability ($\bar{\alpha}$). The CI(SD) results of Amos¹¹ are somewhat smaller than our CI(SD) results for two reasons. First, he computed the polarizability parameters from the induced dipole moments instead of energy differences. We also obtain somewhat smaller β and β' values when we use induced dipole moments, but in cases where the Hellmann-Feynman theorem is not satisfied, the use of energy differences is preferable.¹⁹ Secondly, Amos truncated the virtual space to the lowest 28 virtual orbitals. Our tests indicate that truncating the virtual space can result in significant and arbitrary changes in the polarizability parameters, particularly the derivatives. The SOPPA results of Oddershede and Svendsen¹³ also seem to agree better with the CASSCF results except for their $\bar{\alpha}'$ that seems anomalously low.

Although the theoretical values of β and β' vary significantly, the results for γ are nearly constant. In particular, the SOPPA results of Oddershede and Svendsen¹² are in excellent agreement with our CI(SD) results, and further indicate that γ increases slowly with increasing frequency of the exciting radiation. The only theoretical value less than three is the APSG results of Kendrick,¹⁰ who obtained an anomalously low value for β' . Hence, it is probable that in the static limit, $\gamma = 3.15 \pm 0.2$.

To quantitatively construct the N₂ Raman spectrum from Eqs. (6)–(8) by evaluating the $\langle \psi_{0J} | \beta | \psi_{1J'} \rangle$ matrix elements numerically, one must know β as a function of r . We have determined β for r values of $r_e - 0.2$ to $r_e + 0.3$ bohr in increments of 0.1 bohr using the [5s 3p 2d] GTO basis and the six-reference CI(SD) calculation based on the natural orbitals of the CASSCF wave function. These results are summarized in Table IV. The six spatial occupancies include all configurations with coefficients greater than 0.06 at all r values. The numerical integration was accomplished by the Numerov-Cooly procedure using a spline representation of the β values in Table IV and the RKR potential¹⁴ of the $X^1\Sigma_g^+$ state including a centrifugal distortion term. The resulting $|\langle \psi_{0J} | \beta | \psi_{1J'} \rangle|^2$ matrix elements, relative to $|\langle \psi_{00} | \beta | \psi_{10} \rangle|^2 = 0.1704$ a.u., are given for even $J \leq 30$ in Table V.

The N₂ 1–0 vibrational-rotational Raman spectrum is shown in Fig. 1, in which the correct J dependence of the matrix elements $\langle \psi_{0J} | \beta | \psi_{1J'} \rangle$ is included. Also shown by horizontal bars in Fig. 1 are the relative intensities if $\langle \psi_{0J} | \beta | \psi_{1J'} \rangle$ were assumed to be indepen-

TABLE III. Comparison with other theoretical calculations.

Description of calculation ^a	Energy	Parameter				
		$\bar{\alpha}$	β	$\bar{\alpha}'$	β'	γ
[6s4p3d1f] Gaussian basis						
Hartree–Fock (HF)	−108.985 764	11.56	5.21	7.15	8.12	3.23
CI(SD)	−109.347 780	11.52	4.74	6.07	7.27	3.18
+quadruples correction		11.62	4.65	5.96	7.06	3.15
This work						
[5s3p2d] Gaussian basis						
CASSCF	−109.055 535	10.83	4.07	5.75	5.88	3.00
+six Ref. CI(SD)	−109.175 371	11.71	4.57	5.98	7.02	3.19
This work						
[6s4p2d] Gaussian basis						
$r_e = 2.068$						
HF		11.43	5.04	7.13	7.88	3.23
GVB		11.09	3.83	5.99	6.19	3.34
Morrison–Hay (Refs. 6 and 7)						
[6s4p3d] Gaussian basis						
$r_e = 2.068$						
HF				7.14	7.86	
APSG	−109.057 3	11.14	4.02	5.62	5.43	2.79
Kendrick (Ref. 10).						
[5s4p2d] Gaussian basis						
HF		11.38	5.30	7.10	8.01	3.13
restricted CI(SD)		11.61	4.32	5.71	6.30	3.02
Amos (Ref. 11)						
50-function STO basis						
TDHF (static)		11.36	4.86	7.10	8.36	3.57
SOPPA (static)		11.29	4.07	4.73	6.12	3.12
SOPPA ($\lambda = 5145$ Å)		11.52	4.20	4.95	6.42	3.17
Oddershede–Svendsen (Refs. 12 and 13)						

^aCalculations are carried out at the experimental equilibrium separation unless otherwise specified.

dent of J . Thus, one sees that a finite value for γ (i.e., vibrational-rotational interactions included) increases the intensity of the O branch relative to the S branch. The Q branch is relatively unaffected by vibrational-rotational interactions. The spectrum in Fig. 1 was constructed for an exciting frequency of 4358 Å and for a temperature of 300 K, but it is emphasized that $\beta(r)$ was determined in the static limit. However, since the magnitude of the vibrational-rotational interactions is inversely proportional to γ , which is rather insensitive to the frequency of the exciting light, the spectrum in

Fig. 1 should be close to that observed experimentally after correcting for the instrumental response as a

TABLE V. Relative anisotropy matrix elements for the O , Q , and S branches.^a

J	O branch	Q branch	S branch
	$ \langle \psi_{0J} \beta \psi_{1J-2} \rangle ^2$	$ \langle \psi_{0J} \beta \psi_{1J} \rangle ^2$	$ \langle \psi_{0J} \beta \psi_{1J+2} \rangle ^2$
0		1.0000	0.9933
2	1.0068	1.0001	0.9846
4	1.0159	1.0002	0.9759
6	1.0252	1.0006	0.9674
8	1.0347	1.0010	0.9591
10	1.0443	1.0015	0.9508
12	1.0541	1.0021	0.9427
14	1.0641	1.0029	0.9348
16	1.0743	1.0037	0.9269
18	1.0846	1.0047	0.9192
20	1.0951	1.0057	0.9115
22	1.1058	1.0069	0.9040
24	1.1167	1.0082	0.8966
26	1.1279	1.0096	0.8893
28	1.1392	1.0111	0.8821
30	1.1507	1.0128	0.8750

TABLE IV. Variation of the polarizability with internuclear distance.^a

$r(\text{bohr})$	$\alpha_{ }$	α_{\perp}	β
1.874 32	12.726	9.414	3.313
1.974 32	13.718	9.798	3.920
2.074 32	14.757	10.186	4.571
2.174 32	15.841	10.576	5.265
2.274 32	16.958	10.965	5.993
2.374 32	18.100	11.348	6.752

^aSix-reference CI(SD) calculation using the natural orbitals of the CASSCF wave function and the [5s3p2d] GTO basis.

^aAll matrix elements are relative to $|\langle \psi_{00} | \beta | \psi_{10} \rangle|^2$. These values are based on spline representation of the data in Table IV.

function of frequency. Each rotational line was assigned a purely Gaussian profile based on the Doppler broadening

$$\Delta\nu = 7.16 \times 10^{-7} \lambda_{00}(\text{\AA}) \sqrt{\frac{T(\text{K})}{M(\text{a.u.})}} \quad (13)$$

The spectra were then convoluted with a Gaussian slit so that they correspond to a spectral resolution of about 0.25 Å.

IV. CONCLUSIONS

A systematic theoretical study of the static polarizability of N₂ is presented. We predict that the parameter $\gamma = r_e \beta'_e / \beta_e$, where β_e is the static polarizability anisotropy, $\alpha_{||} - \alpha_{\perp}$ at r_e , should be 3.15 ± 0.2 , which is larger than two recent experimental estimates.^{4,5} It is shown that a CI(SD) procedure is necessary for quantitative results, and that MCSCF-type calculations systematically underestimate the polarizability parameters by reducing the radial extent of the wave function. The 1-0 vibrational-rotational Raman spectrum of N₂ at 300 K is constructed with and without the effects of rotation to demonstrate the magnitude of the vibrational-rotational corrections.

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