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# Static hyperpolarizability of N<sub>2</sub>

Edet F. Archibong and Ajit J. Thakkar

Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 6E2, Canada

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An extensive investigation is reported of the effects of one-particle basis set selection, electron correlation, and molecular vibrations on the static dipole hyperpolarizability of N<sub>2</sub>. Our vibrationally averaged values of the mean static polarizability  $\bar{\alpha}/e^2 a_0^2 E_H^{-1} = 11.87 \pm 0.12$ , the static polarizability anisotropy  $\Delta\alpha/e^2 a_0^2 E_H^{-1} = 4.70 \pm 0.09$ , and the mean, static, electronic hyperpolarizability  $\bar{\gamma}/e^4 a_0^4 E_H^{-3} = 956 \pm 50$  are in good agreement with experiment. The mean, static, vibronic hyperpolarizability is predicted to be  $\bar{\gamma}^v = 89 e^4 a_0^4 E_H^{-3}$ .

## I. INTRODUCTION

Many nonlinear-optical processes<sup>1</sup> are mediated by the third-order nonlinear susceptibility that is the macroscopic manifestation of the molecular second dipole hyperpolarizability tensor  $\gamma$ . Thus device technology is the driving force for much current research on hyperpolarizabilities. These quantities are not easy to measure. Gas phase electric-field-induced second-harmonic generation (ESHG) measurements yield ratios which must be calibrated against theoretical values for a standard.<sup>2</sup> Helium is the ultimate standard because nearly exact theoretical calculations are available,<sup>3</sup> but N<sub>2</sub> is used as a standard in many experiments.<sup>2</sup>

Hence, it is important to have accurate values of the hyperpolarizability of N<sub>2</sub>. There have been numerous *ab initio* calculations<sup>4-8</sup> as summarized in Table I. It shows that even the static, isotropic average  $\bar{\gamma}$  has not converged to better than 20%.

The purpose of this work is to present an extensive investigation of the effects of one-particle basis set selection, electron correlation, and molecular vibrations on the static hyperpolarizability of N<sub>2</sub>. Hartree atomic units are used throughout.

## II. METHODS

The energy  $E_p$  of a neutral centrosymmetric molecule in a weak, homogeneous electric field  $F$  may be written as<sup>9</sup>

$$E_p = E_0 - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots, \quad (1)$$

in which  $E_0$ ,  $\alpha$ , and  $\gamma$ , respectively, are the energy, dipole polarizability, and second dipole hyperpolarizability tensors of the free molecule. The Greek subscripts denote Cartesian components ( $x$ ,  $y$ , or  $z$ ) and a repeated subscript implies summation over the latter. We chose the  $z$  axis to coincide with the molecular axis so that the origin-independent  $\alpha$  and  $\gamma$  tensors, respectively, have two and three independent components. We report the mean polarizability  $\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$ , the polarizability anisotropy  $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ , the mean hyperpolarizability  $\bar{\gamma} = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$ , and the hyperpolarizability anisotropies

$$\Delta_1\gamma = 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz},$$

$$\Delta_2\gamma = \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}.$$

We use the finite field method,<sup>10</sup> in which components of the various polarizability tensors are obtained from energies of the molecule perturbed by different fields. When field-dependent self-consistent-field (SCF) energies are used, the finite-field method is equivalent to the coupled Hartree-Fock (CHF) procedure.<sup>11,12</sup> True correlation effects are obtained when the field-dependent energies are calculated by a method that allows for electron correlation and starts with the field-dependent SCF wave function as the reference function.<sup>12,13</sup> Good reviews of finite-field calculations exist.<sup>14,15</sup>

We calculated energies by the Møller-Plesset (MP) variant of many-body perturbation theory<sup>16,17</sup> using the Gaussian 90 program.<sup>18</sup> The MP energies and properties computed from them can be written as

$$\begin{aligned} \text{MP2} &= \text{SCF} + \text{D2}, & \text{MP3} &= \text{MP2} + \text{D3}, \\ \text{MP4} &= \text{MP3} + \text{S4} + \text{DQ4} + \text{T4}, \end{aligned} \quad (2)$$

where the numerals indicate order; S, D, T, and Q, respectively, stand for contributions from single, double, triple, and disconnected quadruple substitutions with respect to the zeroth-order, field-dependent SCF wave function, and the renormalization term is included in DQ4. We neglected the computationally expensive triples contribution T4; thus the approximate fourth-order energies we use are denoted as SDQMP4.

Another method that we used to calculate correlated energies is quadratic configuration interaction in the space of single and double substitutions (QCISD).<sup>19</sup> This method can be regarded<sup>20</sup> as an approximation to the coupled cluster method in the same space (CCSD). We also used QCISD(T) energies<sup>19</sup> which are QCISD energies corrected for triple substitutions in a noniterative manner. Many calculations were done at the SCF and MP2 levels, two at the SDQMP4 level, and one at the QCISD and QCISD(T) levels. Only the ten valence electrons were correlated; i.e., the two lowest molecular orbitals were kept doubly occupied.

## III. SCF CALCULATIONS—BASIS SET EFFECTS

We examined 21 basis sets of Gaussian-type functions (GTFs) as detailed in Table II. Each basis set is built on a (17s12p)/[9s7p] set  $S$  which consists of a substrate<sup>21</sup> of (16s11p) GTF contracted to [8s6p] and augmented with a diffuse  $s$ -GTF and a diffuse  $p$ -GTF shell. The basis sets are

TABLE I. Previous hyperpolarizability computations on N<sub>2</sub>. The molecular axis is the *z* axis and the bond lengths used were 2.0744a<sub>0</sub> in Ref. 4, 2.0742a<sub>0</sub> in Ref. 5, and 2.0743a<sub>0</sub> in Refs. 6–8.

Basis	$\gamma_{zzzz}$	$\gamma_{xxxx}$	$\gamma_{xxzz}$	$\bar{\gamma}$
SCF/[6s5p3d] <sup>a</sup>	1180	544	300	766
SCF/[5s4p2d1f] <sup>b</sup>	775	662	240	700
SCF/[6s4p3d1f] <sup>c</sup>	808	563	254	665
SCF/[5s3p2d] <sup>d</sup>	790	660	270	730
SCF/[8s6p4d3f] <sup>e</sup>	795	669	250	716
SCF/[8s6p4d2 f1g] <sup>c</sup>	802	594	252	679
SDQMP4/[6s4p3d1f] <sup>c</sup>	1172	639	319	830
CCSD(T)/[5s3p2d] <sup>d</sup>	1290	860	370	1010
CASMCSCF/[8s6p4d3f] <sup>e</sup>	1162	758	310	885

<sup>a</sup>Maroulis and Bishop (Ref. 4).

<sup>b</sup>Jameson and Fowler (Ref. 5).

<sup>c</sup>Maroulis and Thakkar (Ref. 6).

<sup>d</sup>Sekino and Bartlett (Ref. 7).

<sup>e</sup>Luo *et al.* (Ref. 8).

denoted  $X_{ij}$ , where *i* and *j* are the number of *d*- and *f*-GTF shells, respectively, added to *S*, and *X* is a letter that helps distinguish sets of the same size.

Werner and Meyer<sup>22</sup> demonstrated that at least three sets of *d* GTF are required for accurate polarizability calculations. Our basis set A30 consists of *S* plus an even-tempered set of *d* GTF chosen so that the largest exponent is that of the usual polarization function.<sup>23</sup> The SCF properties computed for the equilibrium bond length  $R_e = 2.0743a_0$  are listed in Table III. We added more diffuse *s* and *p* GTF to obtain the A30*s* and A30*p* sets, respectively. Since the results from the A30, A30*s*, and A30*p* sets are very similar, it is clear that *S* contains enough diffuse *s* and *p* GTF. We tried three other basis sets D30, L30, and V30 that consist of *S* and three *d* GTFs suggested by Dykstra,<sup>24</sup> Langhoff *et al.*,<sup>25</sup> and Visser *et al.*,<sup>26</sup> respectively. Table III shows substantial differences among the SCF polarizabilities obtained from the A30, D30,

TABLE II. Basis sets of spherical GTF for N<sub>2</sub>.

<i>S</i> —(16s11p) (Ref. 21) contracted to [8s6p] + 1s(0.052) + 1p(0.036)
A30— <i>S</i> + 3d(0.8,0.229,0.065)
A30 <i>s</i> —A30 + 1s(0.022)
A30 <i>p</i> —A30 + 1p(0.016)
D30— <i>S</i> + 3d(0.9,0.13,0.02)
L30— <i>S</i> + 3d(0.95,0.26,0.11)
V30— <i>S</i> + 3d(0.9,0.3,0.1)
A40—A30 + 1d(0.019)
L40—L30 + 1d(0.019)
V40—V30 + 1d(0.033)
V50 <i>d</i> —V40 + 1d(0.011)
V50 <i>t</i> —V40 + 1d(2.7)
V31— <i>S</i> + 3d(0.9,0.3,0.1) + 1f(0.1)
V41 <i>t</i> —V40 + 1f(0.3)
V41 <i>d</i> —V40 + 1f(0.1)
V42— <i>S</i> + 4d(0.9,0.3,0.1,0.033) + 2f(0.3,0.1)
V52—V42 + 1d(2.4)
V43 <i>t</i> —V42 + 1f(0.9)
V43 <i>d</i> —V42 + 1f(0.03)
V53 <i>t</i> —V42 + 1d(2.4) + 1f(0.9)
V53 <i>d</i> —V42 + 1d(2.4) + 1f(0.03)
V54— <i>S</i> + 5d(2.4,0.9,0.3,0.1,0.033) + 4f(0.9,0.3,0.1,0.03)

L30, and V30 basis sets, suggesting that these sets are not yet saturated with *d* GTF.

Thus we examined three sets with four *d* GTFs. The variation among the SCF properties obtained with A40, L40, and V40 is much smaller, indicating that these sets are close to saturation with *d* GTF. We selected V40 for further extension since it provides the overall best (largest<sup>27</sup>) values of  $\bar{\alpha}$  and  $\bar{\gamma}$ . A comparison of the V40, V50*d*, and V50*t* properties shows that a fifth *d* GTF does not make much difference, but, if used, should be tight rather than diffuse.

The role of *f* GTF is considered next with V31, V41*t*, and V41*d*. The results confirm the previous finding<sup>5</sup> that *f* GTFs make a substantial contribution to the transverse component  $\gamma_{xxxx}$ , and that the more diffuse *f* GTF is more important than the tighter one. Clearly the basis set V31 is a much better compromise between size and accuracy than V40, V50*d*, or V50*t*. A small improvement at the SCF level is obtained with V42. Various extensions of V42 were tried, but Table III and Fig. 1 show that all basis sets larger than V42 predict essentially the same SCF value of  $\bar{\gamma}$ . The SCF energy and quadrupole moment  $Q_2$  in the [9s7p5d4f] basis set V54 are close to the numerical Hartree–Fock limit values<sup>28</sup> of  $-108.993\ 81E_H$  and  $-0.931\ e a_0^2$ , respectively. Moreover, all the SCF components of the  $\gamma$  tensor in the V54 basis agree very closely with those obtained by Luo *et al.*<sup>8</sup> with the [8s6p4d3f] basis denoted A3 by them. Since Luo *et al.*<sup>8</sup> have found that *g* GTFs do not contribute significantly to the hyperpolarizability of N<sub>2</sub>, we conclude that the CHF limit is  $\bar{\gamma} = 717 \pm 5 e^4 a_0^4 E_H^{-3}$ .

#### IV. ELECTRON CORRELATION

Table IV lists MP2 polarizabilities and hyperpolarizabilities of N<sub>2</sub> in all ten basis sets that contain at least one *f* GTF. On the basis of the SCF results, we ignore V41*t*, which has a nonoptimal choice of exponent for the *f* GTF. Figure 1 shows that the other values of  $\bar{\gamma}/e^4 a_0^4 E_H^{-3}$  lie between 874 and 901, a spread of only 3% around the best MP2 value  $\bar{\gamma} = 880 e^4 a_0^4 E_H^{-3}$  obtained in the largest V54 basis set. As expected from previous experience,<sup>6</sup> the anisotropies are converged to a lesser degree. The MP2 values of  $\Delta_1 \gamma/e^4 a_0^4 E_H^{-3}$  lie between 1444 and 1542, and the MP2 values of  $\Delta_2 \gamma/e^4 a_0^4 E_H^{-3}$  range from 58 to 103.

Next, consider higher order effects of electron correlation. Table V lists polarizabilities and hyperpolarizabilities calculated at the SDQMP4 level in the V42 basis set that contains 128 CGTFs, and SDQMP4, QCISD, and QCISD(T) properties in the smaller V31 basis set (104 CGTFs). The SDQMP4 values of  $\bar{\gamma}$  are smaller than their MP2 counterparts by 33 and  $36 e^4 a_0^4 E_H^{-3}$  in the V31 and V42 basis sets, respectively. Moreover, Table V shows that there are significant differences between the SDQMP4 and QCISD results, confirming the slow convergence of the MP series noted previously for the polarizabilities of a few small molecules containing triple bonds.<sup>29</sup> Curiously,  $|\gamma(\text{MP2}) - \gamma(\text{QCISD})| < |\gamma(\text{SDQMP4}) - \gamma(\text{QCISD})|$ , whereas the opposite is true for the  $\alpha$  tensor. A comparison of the QCISD and QCISD(T) values in Table V shows that triple substitutions make a significant contribution to the  $\gamma$  tensor as found earlier in neon<sup>30,31</sup> and molecular nitrogen.<sup>7</sup>

TABLE III. SCF properties of N<sub>2</sub> at  $R=2.0743a_0$ .

Basis	$E+100$	$-Q_2$	$\bar{\alpha}$	$\Delta\alpha$	$\gamma_{zzzz}$	$\gamma_{xxxx}$	$\gamma_{xxzz}$	$\bar{\gamma}$
A30	-8.982 46	0.9386	11.525	5.231	778.0	588.4	252.7	671.6
A30s	-8.982 46	0.9387	11.525	5.231	780.4	589.4	252.8	672.7
A30p	-8.982 46	0.9387	11.525	5.231	778.6	590.0	253.2	672.9
D30	-8.984 20	0.9353	11.445	5.250	762.1	561.6	254.9	655.9
L30	-8.985 88	0.9233	11.539	5.193	772.1	516.9	243.1	624.6
V30	-8.985 00	0.9347	11.540	5.191	772.0	548.9	248.4	645.9
A40	-8.982 46	0.9384	11.528	5.227	780.6	576.6	252.1	665.3
L40	-8.985 89	0.9232	11.542	5.188	774.5	538.6	248.1	640.6
V40	-8.985 01	0.9343	11.541	5.192	785.1	567.9	255.0	663.9
V50d	-8.985 01	0.9342	11.541	5.191	786.0	568.3	255.2	664.5
V50t	-8.989 33	0.9105	11.548	5.179	789.1	568.1	254.7	664.6
V31	-8.985 03	0.9349	11.542	5.192	785.6	646.9	244.7	697.9
V41t	-8.985 37	0.9381	11.545	5.204	791.2	592.8	250.8	675.0
V41d	-8.985 03	0.9344	11.543	5.190	788.8	670.8	249.0	714.8
V42	-8.985 48	0.9346	11.547	5.189	800.0	674.4	247.6	717.8
V52	-8.989 69	0.9171	11.554	5.181	796.7	672.9	248.2	716.8
V43t	-8.988 33	0.9450	11.558	5.208	804.1	668.4	249.5	716.9
V43d	-8.985 49	0.9344	11.547	5.188	799.8	670.0	247.8	715.5
V53t	-8.991 94	0.9287	11.561	5.198	800.5	666.3	250.1	715.6
V53d	-8.989 70	0.9170	11.554	5.180	796.3	671.1	248.6	716.0
V54	-8.991 95	0.9287	11.561	5.198	798.9	668.7	250.8	717.0

A better estimate of the correlated values of the  $\alpha$  and  $\gamma$  tensors can be obtained by assuming additivity of basis set and electron correlation effects. Thus, Table V lists the hybrid estimate

Hybrid=QCISD(T)/V31+SDQMP4/V42

$$-\text{SDQMP4}/V31+\text{MP2}/V54-\text{MP2}/V42. \quad (3)$$

Equation (3) combines our MP2 results in the large V54 basis set (166 CGTFs) with the difference between the SDQMP4 and MP2 values in the smaller V42 basis set (128 CGTFs), and the difference between QCISD(T) and SDQMP4 in the more modest V31 basis set (104 CGTFs). The hybrid estimates are remarkably close to the QCISD(T)/V31 values.

Our hybrid mean polarizability  $\bar{\alpha}/e^2a_0^2E_H^{-1}=11.81$  is in good agreement with our previous SDQMP4 calculation<sup>6</sup> of 11.68, and the somewhat lower complete active space, multiconfiguration self-consistent field (CASMCSCF) calculation<sup>8</sup> of 11.61. Similarly, our hybrid value of the polarizability anisotropy  $\Delta\alpha/e^2a_0^2E_H^{-1}=4.63$  is in good agreement with our previous SDQMP4 calculation<sup>6</sup> of 4.65, but

TABLE IV. MP2 polarizabilities and hyperpolarizabilities of N<sub>2</sub> at  $R=2.0743a_0$ .

Basis	$\bar{\alpha}$	$\Delta\alpha$	$\gamma_{zzzz}$	$\gamma_{xxxx}$	$\gamma_{xxzz}$	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
V31	11.550	4.212	1190	740.5	311.5	882.1	1542	61
V41d	11.553	4.211	1190	768.2	315.8	900.4	1444	63
V42	11.595	4.167	1200	762.0	309.9	894.4	1483	103
V52	11.574	4.178	1188	754.7	310.9	888.8	1477	77
V43t	11.558	4.167	1190	748.2	310.6	885.6	1510	75
V43d	11.595	4.166	1202	757.9	313.2	895.1	1513	80
V53t	11.534	4.176	1173	739.4	307.0	874.5	1481	70
V53d	11.574	4.177	1191	752.7	312.1	889.2	1497	71
V54	11.534	4.175	1179	742.9	310.6	880.4	1496	58

the CASMCSCF computation<sup>8</sup> of 4.34 seems a little low. Older calculations are reviewed in Refs. 6 and 8. We think our hybrid values are more likely to be too high than too low, and estimate the uncertainties in our hybrid  $\bar{\alpha}$  and  $\Delta\alpha$  to be no more than 1% and 2%, respectively.

There is a much larger uncertainty in the dipole hyperpolarizability  $\gamma$ . On the basis of Table IV and Fig. 1, we think that our MP2/V54 value of  $\bar{\gamma}/e^4a_0^4E_H^{-3}$  has an uncertainty of no more than  $\pm 25$ . On the basis of our experience with correlated hyperpolarizability calculations,<sup>6,30,32-35</sup> we guess that the higher order correction (hybrid-MP2/V54) cannot be in error by more than one-third. Thus we estimate that  $\bar{\gamma}/e^4a_0^4E_H^{-3}=946\pm 50$  for N<sub>2</sub> at its equilibrium bond length of  $2.0743a_0$ , with the estimate more likely to be too high than too low. A graphical comparison with other values is made in Fig. 2. Our older SDQMP4 value<sup>6</sup> of 830 is too low because of the use of a nonoptimal  $f$  GTF, and Sekino

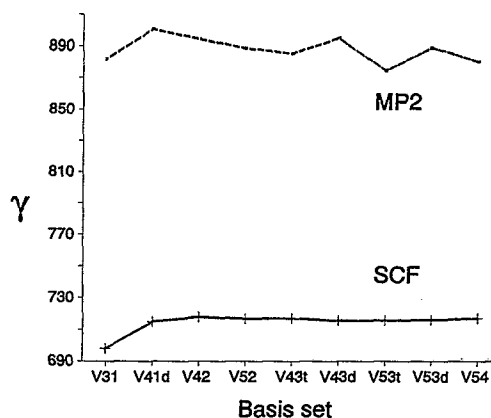
FIG. 1. Isotropic, static hyperpolarizability of N<sub>2</sub> at  $R_e=2.0743a_0$  as predicted by various basis sets at the SCF and MP2 levels.

TABLE V. Highly correlated and experimental polarizabilities and hyperpolarizabilities of N<sub>2</sub> at  $R=2.0743a_0$ .

Method	$\bar{\alpha}$	$\Delta\alpha$	$\gamma_{zzzz}$	$\gamma_{xxxx}$	$\gamma_{xxzz}$	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
SDQMP4/V31	11.664	4.693	1109	724	301	849	1340	26
SDQMP4/V42	11.705	4.656	1115	743	299	858	1270	65
QCISD/V31	11.721	4.671	1201	772	319	907	1470	60
QCISD(T)/V31	11.827	4.661	1273	802	336	951	1620	62
Hybrid <sup>b</sup>	11.807	4.632	1258	802	335	946	1563	56
Averaged <sup>b</sup>	11.81	4.70	1272	810	339	956	1586	54
Experiment	11.74 <sup>c</sup>	4.59 <sup>d</sup>				917 <sup>e</sup>		
		4.694 <sup>f</sup>						

<sup>a</sup>QCISD(T)/V31+SDQMP4/V42-SDQMP4/V31+MP2/V54-MP2/V42.<sup>b</sup>Hybrid values above plus corrections for zero point vibrational averaging.<sup>c</sup>Constrained oscillator strength distribution (Ref. 41).<sup>d</sup>Constrained oscillator strength distribution (Ref. 43).<sup>e</sup>Electric-field-induced second-harmonic generation (Ref. 2).<sup>f</sup>Kerr effect (Ref. 42).

and Bartlett's CCSD(T) value<sup>7</sup> of 1010 is a bit too high presumably because of the smaller basis set they used. Luo *et al.*'s CASMCSCF value<sup>8</sup> of 885 is marginally outside our estimate and, we believe, a bit too low because of an insufficiently large active space.

## V. VIBRATIONAL EFFECTS

All the calculated properties need to be averaged over the zero point vibrational state. These zero point vibrational corrections are known<sup>6,8</sup> to be small for N<sub>2</sub>. Therefore, the averaging of the bond length dependent properties  $P(R)$  was performed by using a MacLaurin expansion truncated after the linear term

$$\langle 0|P(R)|0\rangle \approx P(R_e) + \langle 0|R-R_e|0\rangle \left( \frac{\partial P}{\partial R} \right)_{R=R_e}, \quad (4)$$

in which  $|0\rangle$  is the wave function for the *ground* vibrational state. The partial derivative in Eq. (4) was approximated by a central, three point finite difference using the SDQMP4/V42 results for  $R=R_e=2.0743a_0$ , and additional SDQMP4/

V42 calculations (not tabulated) made at  $R=2.068$  and  $2.0806a_0$ . The vibrational matrix element appearing in Eq. (4) was computed from a Numerov<sup>36</sup> solution of the vibrational Schrödinger equation using a Rydberg-Klein-Rees interatomic potential<sup>37</sup> calculated by us from experimental spectroscopic constants.<sup>38</sup>

The zero point vibrational corrections to  $\bar{\alpha}$  and  $\Delta\alpha$  were found to be 0.06 and  $0.07e^2a_0^2E_H^{-1}$ , respectively, and the zero point vibrational corrections to  $\gamma_{zzzz}$ ,  $\gamma_{xxxx}$ ,  $\gamma_{xxzz}$ , and  $\bar{\gamma}$  were found to be 14, 8, 4, and  $10e^4a_0^4E_H^{-3}$ , respectively, in good agreement with previous estimates<sup>6,8</sup> where available.

There are also vibronic or "pure vibrational" contributions to be considered. The vibronic dipole polarizability vanishes for a homonuclear diatomic molecule, but the vibronic hyperpolarizability does not. The components  $\gamma_{aabb}$  of the latter are given by<sup>39</sup>

$$\gamma_{aabb}^v = c \sum_{k=1} \frac{\langle 0|\alpha_{aa}|k\rangle \langle 0|\alpha_{bb}|k\rangle}{(\epsilon_k - \epsilon_0)}, \quad (5)$$

in which  $\epsilon_k$  is the energy of the vibrational state  $|k\rangle$  with quantum number  $v=k$ , the constant  $c=6$  for the longitudinal ( $a=b=z$ ) and transverse ( $a=b=x$ ) components, and  $c=2$  for the mixed ( $a=x, b=z$ ) component. The matrix elements in Eq. (5) were evaluated by using a MacLaurin expansion truncated after the linear term

$$\langle 0|P(R)|k\rangle \approx P(R_e) + \langle 0|R-R_e|k\rangle \left( \frac{\partial P}{\partial R} \right)_{R=R_e}. \quad (6)$$

The quantities on the right-hand side of Eq. (6) were evaluated in the manner described below Eq. (4). Only one term ( $k=1$ ) made a significant contribution to the sum over states in Eq. (5).

The components of the vibronic hyperpolarizability tensor  $\gamma_{zzzz}^v$ ,  $\gamma_{xxxx}^v$ , and  $\gamma_{xxzz}^v$ , and the mean  $\bar{\gamma}^v$  were found to be 253, 29, 28, and  $89e^4a_0^4E_H^{-3}$ , respectively, in fine agreement with the estimates of 221, 26, 28, and  $80e^4a_0^4E_H^{-3}$  obtained by Bishop and Lam<sup>40</sup> in the harmonic approximation.

## VI. A COMPARISON WITH EXPERIMENT

Adding the zero point vibrational corrections to our hybrid values leads to vibrationally averaged values that can be compared with experiment. Our value of  $\bar{\alpha}/e^2a_0^2E_H^{-1}=11.87\pm 0.12$  (see Table V) is in good agreement with the best estimate of  $11.74\pm 0.12$  obtained<sup>41</sup> from constrained oscillator strength distributions (DOSD). Our value of  $\Delta\alpha/e^2a_0^2E_H^{-1}=4.70\pm 0.09$  is in nearly perfect agreement with the Kerr effect value<sup>42</sup> of 4.694, and in good agreement with the constrained DOSD value<sup>43</sup> of  $4.59\pm 0.05$ .

Our estimate of the vibrationally averaged electronic hyperpolarizability  $\bar{\gamma}/e^4a_0^4E_H^{-3}=956\pm 50$  can be compared directly with the most recent experimental estimate<sup>2</sup> of  $917\pm 10$  because the latter has the vibronic component removed. The agreement is about as good as we believe can be achieved consistently for the second hyperpolarizability of small molecules with current computational technology.

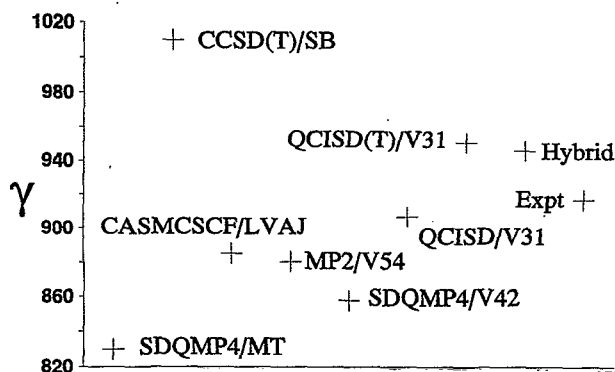


FIG. 2. Isotropic, static hyperpolarizability of N<sub>2</sub> at  $R_e=2.0743a_0$ . The SDQMP4/MT value is from Maroulis and Thakkar (Ref. 6), the CCSD(T)/SB value is from Sekino and Bartlett (Ref. 7), the CASMCSCF/LVAJ value is from Luo *et al.* (Ref. 8), the experimental value is from Shelton (Ref. 2), and the remaining values are from this work.

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- <sup>1</sup>Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984).
- <sup>2</sup>D. P. Shelton, *Phys. Rev. A* **42**, 2578 (1990).
- <sup>3</sup>D. M. Bishop and J. Pipin, *J. Chem. Phys.* **91**, 3549 (1989).
- <sup>4</sup>G. Maroulis and D. M. Bishop, *Mol. Phys.* **58**, 273 (1986).
- <sup>5</sup>C. J. Jameson and P. W. Fowler, *J. Chem. Phys.* **85**, 3432 (1986).
- <sup>6</sup>G. Maroulis and A. J. Thakkar, *J. Chem. Phys.* **88**, 7623 (1988); (Erratum) **89**, 6558 (1988).
- <sup>7</sup>H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **98**, 3022 (1993); **94**, 3665 (1991).
- <sup>8</sup>Y. Luo, O. Vahtras, H. Ågren, and P. Jørgensen, *Chem. Phys. Lett.* **205**, 555 (1993).
- <sup>9</sup>A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
- <sup>10</sup>H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, 34 (1965).
- <sup>11</sup>M. Cohen and A. Dalgarno, *Rev. Mod. Phys.* **35**, 506 (1963).
- <sup>12</sup>T. C. Caves and M. Karplus, *J. Chem. Phys.* **50**, 3649 (1969).
- <sup>13</sup>L. Adamowicz and A. J. Sadlej, *Chem. Phys. Lett.* **53**, 377 (1978).
- <sup>14</sup>C. E. Dykstra, *Ab initio Calculation of the Structures and Properties of Molecules* (Elsevier, Amsterdam, 1988).
- <sup>15</sup>M. Urban, I. Cernusak, V. Kello and J. Noga, *Methods Comp. Chem.* **1**, 117 (1987).
- <sup>16</sup>R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- <sup>17</sup>W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).
- <sup>18</sup>M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian 90, revision J, Gaussian, Inc., Pittsburgh, 1990.
- <sup>19</sup>J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- <sup>20</sup>J. Paldus, J. Cizek, and B. Jeziorski, *J. Chem. Phys.* **90**, 4356 (1989); J. A. Pople, M. Head-Gordon, and K. Raghavachari, *ibid.* **90**, 4635 (1989); G. E. Scuseria and H. F. Schaefer, *ibid.* **90**, 3700 (1989); K. Raghavachari, J. A. Pople, E. S. Replogle, and M. Head-Gordon, *J. Phys. Chem.* **94**, 5579 (1990); K. Raghavachari, *Annu. Rev. Phys. Chem.* **42**, 615 (1991).
- <sup>21</sup>H. Partridge, *J. Chem. Phys.* **90**, 1043 (1989); NASA Technical Memorandum 101044, Ames Research Center, Moffett Field, CA, 1989.
- <sup>22</sup>H. J. Werner and W. Meyer, *Mol. Phys.* **31**, 855 (1976).
- <sup>23</sup>T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), pp. 1–27.
- <sup>24</sup>C. E. Dykstra, *J. Chem. Phys.* **82**, 4120 (1985).
- <sup>25</sup>S. R. Langhoff, C. W. Bauschlicher, and D. P. Chong, *J. Chem. Phys.* **78**, 5287 (1983).
- <sup>26</sup>F. Visser, P. E. S. Wormer, and P. Stam, *J. Chem. Phys.* **79**, 4973 (1983).
- <sup>27</sup>S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).
- <sup>28</sup>D. Sundholm, P. Pykkö, and L. Laaksonen, *Mol. Phys.* **56**, 1411 (1985); See also Table 7 of P. Pykkö, D. Sundholm, and L. Laaksonen, *ibid.* **60**, 597 (1987).
- <sup>29</sup>P. W. Fowler and G. H. F. Dierksen, *Chem. Phys. Lett.* **167**, 105 (1990).
- <sup>30</sup>G. Maroulis and A. J. Thakkar, *Chem. Phys. Lett.* **156**, 87 (1989).
- <sup>31</sup>J. E. Rice, G. E. Scuseria, T. J. Lee, P. R. Taylor, and J. Almlof, *Chem. Phys. Lett.* **191**, 23 (1992), and references cited therein.
- <sup>32</sup>G. Maroulis and A. J. Thakkar, *J. Chem. Phys.* **90**, 366 (1989); **93**, 652 (1990); **93**, 4164 (1990); **95**, 9060 (1991).
- <sup>33</sup>A. J. Thakkar, *Phys. Rev. A* **40**, 1130 (1989).
- <sup>34</sup>E. F. Archibong and A. J. Thakkar, *Chem. Phys. Lett.* **173**, 579 (1990); *Phys. Rev. A* **44**, 5478 (1991).
- <sup>35</sup>E. F. Archibong and A. J. Thakkar, *Chem. Phys. Lett.* **201**, 485 (1993).
- <sup>36</sup>R. J. LeRoy, Chemical Physics Research Report CP-330, University of Waterloo, Ontario, 1991.
- <sup>37</sup>R. Rydberg, *Z. Phys.* **73**, 376 (1931); **80**, 514 (1933); O. Klein, *ibid.* **76**, 226 (1932); A. L. G. Rees, *Proc. Phys. Soc.* **59**, 998 (1947).
- <sup>38</sup>A. Lofthus and P. H. Krupenie, *J. Phys. Chem. Ref. Data* **6**, 113 (1977).
- <sup>39</sup>D. M. Bishop, *Rev. Mod. Phys.* **62**, 343 (1990).
- <sup>40</sup>D. M. Bishop and B. Lam, *Chem. Phys. Lett.* **134**, 283 (1987).
- <sup>41</sup>G. D. Zeiss, W. J. Meath, J. C. F. MacDonald, and D. J. Dawson, *Can. J. Phys.* **55**, 2080 (1977).
- <sup>42</sup>A. D. Buckingham, M. P. Bogaard, D. A. Dunmur, G. P. Hobbs, and B. J. Orr, *Trans. Faraday Soc.* **66**, 1548 (1970).
- <sup>43</sup>W. J. Meath and A. Kumar, *Int. J. Quantum Chem. Symp.* **24**, 501 (1990).