

# Quadrupole moment function and absolute infrared quadrupolar intensities for N<sub>2</sub>

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High level *ab initio* methods have been used to calculate values of the quadrupole moment of the ground  $X^1\Sigma_g^+$  state of N<sub>2</sub> on a dense radial mesh spanning the interval of 0.8–12.1 a.u. Detailed convergence tests indicate that the resulting equilibrium values of the quadrupole moment  $\Theta_e = -1.1273$  a.u. and its first radial derivative  $d\Theta(R)/dR|_e = 0.9604$  a.u. have absolute uncertainties of 0.3% and 0.8%, respectively, and are more accurate than the best experimental values of these quantities. The calculated quadrupole moment function, together with a recently reported accurate analytic empirical potential energy function [Le Roy *et al.*, *J. Chem. Phys.* **125**, 164310 (2006)], is used to generate values of the radial matrix elements determining the absolute intensities of infrared vibration-rotation transitions of ground-state N<sub>2</sub>, which take full account of vibration-rotation interactions. These results should improve the reliability of the interpretations of N<sub>2</sub> contributions to infrared atmospheric spectra. © 2007 American Institute of Physics.  
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## I. INTRODUCTION

Since its first detection in 1981 by Goldman *et al.*<sup>1</sup> the infrared quadrupole absorption spectrum of N<sub>2</sub> has come to be an integral part of retrievals from atmospheric spectra. However, early interpretations of such spectra were based on radial quadrupole matrix elements based on a harmonic oscillator model for the potential function, and ignored the effects of vibration-rotation interaction.<sup>2,3</sup> In recent work, Goldman *et al.*<sup>4</sup> reported the determination of line parameters for the 1-0 infrared quadrupole transition which use the analytic Herman-Wallis intensity factor expressions of Tipping and Ogilvie<sup>5</sup> to take account of the effects of the vibrational anharmonicity and vibration-rotation interaction on such intensities. However, the quadrupole moment properties used in their formulas were based on experimental values of the average quadrupole moment<sup>6</sup> and quadrupole moment derivative<sup>3</sup> which had estimated uncertainties of 5.5% and 4.2%, respectively. These uncertainties are far larger than those associated with modern *ab initio* calculations of such properties (see, e.g., Lawson and Harrison<sup>7</sup>). Moreover, while the semiclassical expressions of Tipping and Ogilvie may be expected to be fairly accurate for even moderately high rotational levels of the fundamental band, they will be less reliable for high overtones or hot bands.

In view of the above, the present work begins by determining an accurate new *ab initio* distance-dependent quadrupole moment function for N<sub>2</sub>. Equilibrium values of the average polarizability and polarizability anisotropy are also calculated at the same level of theory. The quadrupole moment function is then combined with numerical wave functions generated from an accurate new analytic potential energy function<sup>8</sup> for N<sub>2</sub> to calculate *J*-dependent matrix elements for a range of N<sub>2</sub> infrared quadrupole transitions.

## II. AB INITIO CALCULATION OF THE QUADRUPOLE MOMENT AND POLARIZABILITIES OF N<sub>2</sub>

### A. Computational details

All of our *ab initio* calculation were performed using the MOLPRO package.<sup>9</sup> The following methods were employed in these calculations: Hartree-Fock self-consistent field (SCF), multiconfiguration self-consistent field (MCSCF),<sup>10,11</sup> and methods that include dynamic electron correlation effects: internally contracted multireference configuration interaction<sup>12</sup> (MR-CI) and size-extensive modifications of MR-CI [multireference averaged quadratic coupled-cluster<sup>13</sup> (MR-AQCC) and multireference averaged coupled-pair functional<sup>14</sup> (MR-ACPF) methods]. The reference wave functions in the MR-CI, MR-AQCC, and MR-ACPF calculations are all taken to be the natural orbitals obtained from the complete active space self-consistent-field (CASSCF) wave functions.<sup>10,11</sup> Ten active electrons and eight active orbitals were used. The 1s-type core orbitals of nitrogen were fully optimized, while being constrained to be doubly occupied and excluded from the full valence active space, which is denoted as MCSCF(10,8).

Five families of basis sets were considered. To determine the effect of diffuse basis functions, which is important because the electric quadrupole moment operator is quadratic in the the electron coordinates ( $r_i$ ), a series of augmented correlation-consistent polarized basis sets, denoted by aug-cc-pVXZ ( $X=D-6$ ),<sup>15,16</sup> the doubly augmented correlation-consistent polarized basis sets denoted by daug-cc-pVXZ ( $X=D-5$ ),<sup>17</sup> and the the triply augmented correlation-consistent polarized basis sets denoted by taug-cc-pVXZ ( $X=D-5$ ),<sup>17</sup> were all employed in our calculations. As a reference, correlation-consistent polarized basis sets without augmented functions, denoted by cc-pVXZ ( $X=D-6$ ),<sup>15</sup> are also used. To determine the effect of core correlation, calcu-

TABLE I. Calculated values of  $\Theta_e$  for  $N_2$  at the experimental equilibrium distance  $R_e=2.074\ 32$  a.u.

Method	X	Basis set						
		pVXZ				aug-cc-pCVXZ		
		cc	aug-cc	daug-cc	taug-cc	Contracted	Uncontracted	Uncontracted DK
HF	D	-1.1273	-0.8949	-0.9161	-0.9179	-0.8946		
	T	-1.0187	-0.9265	-0.9286	-0.9299	-0.9206		
	Q	-0.9734	-0.9262	-0.9280	-0.9287	-0.9256		
	5	-0.9612	-0.9298	-0.9307	-0.9307	-0.9298		
	6	-0.9457	-0.9309					
CASSCF	D	-1.3280	-1.1535	-1.1784	-1.1805	-1.1559	-1.1604	-1.1565
	T	-1.2585	-1.1868	-1.1893	-1.1908	-1.1808	-1.1779	-1.1740
	Q	-1.2271	-1.1872	-1.1889	-1.1896	-1.1866	-1.1866	-1.1827
	5	-1.2193	-1.1907	-1.1914	-1.1915	-1.1906	-1.1906	-1.1867
	6	-1.2049	-1.1916					
MR-CI	D	-1.3553	-1.1261	-1.1557	-1.1576	-1.1278	-1.1316	-1.1278
	T	-1.2361	-1.1342	-1.1394	-1.1412	-1.1351	-1.1319	-1.1281
	Q	-1.1849	-1.1321	-1.1344	-1.1351	-1.1386	-1.1385	-1.1347
	5	-1.1701	-1.1336	-1.1345	-1.1346	-1.1410	-1.1410	-1.1372
	6	-1.1507	-1.1337					
MR-AQCC	D	-1.3622	-1.1244	-1.1546	-1.1566	-1.1257	-1.1292	-1.1254
	T	-1.2387	-1.1276	-1.1334	-1.1351	-1.1269	-1.1235	-1.1198
	Q	-1.1834	-1.1249	-1.1274	-1.1281	-1.1291	-1.1290	-1.1253
	5	-1.1671	-1.1259	-1.1269	-1.1270	-1.1311	-1.1311	<b>-1.1273</b>
	6	-1.1457	-1.1260					
MR-ACPF	D	-1.3643	-1.1239	-1.1543	-1.1563	-1.1254	-1.1288	-1.1251
	T	-1.2397	-1.1253	-1.1314	-1.1330	-1.1251	-1.1217	-1.1180
	Q	-1.1828	-1.1224	-1.1250	-1.1257	-1.1270	-1.1269	-1.1232
	5	-1.1662	-1.1233	-1.1243	-1.1244	-1.1288	-1.1288	-1.1251
	6	-1.1440	-1.1233					

lations were also performed using the augmented correlation-consistent core and valence polarization basis sets of Woon and Dunning, denoted by aug-cc-pCVXZ ( $X=D-5$ ).<sup>18</sup>

The quadrupole moment calculated here is the traceless moment defined by Buckingham.<sup>19</sup> For a homonuclear diatomic molecule, it is written as

$$\Theta_{zz} \equiv \Theta = -\frac{1}{2} \sum_{i=1}^{N_e} (3z_i^2 - r_i^2) + \frac{1}{2} ZR^2, \quad (1)$$

where  $Z$  is the atomic number of the nuclei and  $R$  is the internuclear separation, and the electron coordinates  $z_i$  and  $r_i$  are expressed relative to an origin at the bond mid-point. For linear molecules the  $\Theta$  tensor is diagonal and the relationship  $\Theta_{zz} = -2\Theta_{yy} = -2\Theta_{xx}$  is fulfilled. As it is  $\Theta_{zz}$  that matters experimentally, only this component is reported below. Except where explicitly noted otherwise, atomic units are used throughout.

If the radial dependence of the quadrupole moment of  $N_2$  is represented by a Taylor series expansion about the equilibrium distance  $R_e$ ,

$$\Theta(R) = \sum_k c_k (R - R_e)^k, \quad (2)$$

then its  $k$ th order derivative at  $R_e$  is represented as

$$\left( \frac{d^k \Theta}{dR^k} \right)_e = c_k k!. \quad (3)$$

At all levels of theory, values of the leading quadrupole moment derivatives at  $R_e$  were obtained by performing calculations at eleven grid points defined by the increments  $\Delta R \equiv (R - R_e)/a_0 = 0.0, \pm 0.1, \pm 0.2, \pm 0.3, \pm 0.4$ , and  $\pm 0.5$ , and performing least-squares fits to Eq. (2).

The static electric polarizability was calculated using the finite-field method,<sup>20</sup> which has been explained in detail in a previous work.<sup>21</sup> Seven weak electric fields of strength, 0.000, 0.002, 0.004, 0.005, 0.006, 0.008 and 0.010 a.u., were used to perturb molecular energies. Least-squares fits to an even-power polynomial expansion in the electric field strength were then used to determine reliable values of the leading coefficient, which defines the  $\alpha_{zz}$  and  $\alpha_{xx}$  Cartesian components of the polarizability associated with the alignment of the electric field along and perpendicular to the molecular axis, respectively. The anisotropy of the polarizability is  $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ , while the isotropic average polarizability is  $\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$ .

## B. *Ab initio* results

Table I lists values of the quadrupole moment of  $N_2$  at the experimental equilibrium bond length ( $R_e = 1.097\ 68$  Å)

TABLE II. Spectroscopic parameters for ground N<sub>2</sub> were calculated at MR-AQCC and MR-ACPF levels with uncontracted aug-cc-pCVSZ basis set including scalar relativistic correction using Douglas-Kroll relativistic Hamiltonian, and then compared with corresponding experimental values.

Levels	G <sub>v</sub> -G <sub>0</sub>			B		
	Expt.	MR-AQCC	MR-ACPF	Expt.	MR-AQCC	MR-ACPF
0	0.00	0.00	0.00	1.989 59	-0.000 50	-0.001 20
1	2 329.91	0.50	-1.37	1.972 22	-0.000 46	-0.001 18
2	4 631.17	1.05	-2.74	1.954 79	-0.000 42	-0.001 16
3	6 903.72	1.64	-4.11	1.937 32	-0.000 38	-0.001 15
4	9 147.54	2.29	-5.48	1.919 79	-0.000 35	-0.001 14
5	11 362.59	2.98	-6.84	1.902 20	-0.000 31	-0.001 13
6	13 548.81	3.74	-8.19	1.884 55	-0.000 28	-0.001 12
7	15 706.18	4.54	-9.55	1.866 84	-0.000 24	-0.001 11
8	17 834.62	5.41	-10.89	1.849 05	-0.000 21	-0.001 10
9	19 934.09	6.34	-12.23	1.831 20	-0.000 17	-0.001 09
10	22 004.52	7.34	-13.57	1.813 27	-0.000 13	-0.001 08
11	24 045.86	8.39	-14.89	1.795 27	-0.000 09	-0.001 07
12	26 058.03	9.51	-16.22	1.777 17	-0.000 04	-0.001 06
13	28 040.94	10.70	-17.55	1.758 99	0.000 00	-0.001 05
14	29 994.52	11.95	-18.87	1.740 71	0.000 05	-0.001 03
15	31 918.65	13.25	-20.21	1.722 32	0.000 11	-0.001 02
16	33 813.23	14.63	-21.54	1.703 81	0.000 17	-0.001 00
17	35 678.10	16.07	-22.88	1.685 18	0.000 24	-0.000 97
18	37 513.11	17.61	-24.20	1.666 41	0.000 31	-0.000 93
19	39 318.06	19.26	-25.47	1.647 47	0.000 41	-0.000 88
	RMS	10.06	15.38		0.000 28	0.001 08
	R <sub>e</sub> /Å	1.097 68	0.000 14	0.000 33		
	D <sub>e</sub> /eV	9.899 5	-0.044 8	-0.066 0		

calculated using a variety of basis sets and computational methods. Relative to the results yielded by the MR-CI, MR-AQCC, and MR-ACPF methods, which take account of the dynamic correlation, the values of  $\Theta_e$  obtained at the SCF level are about 0.2 a.u. (or 20%) too high, while the CASSCF results are approximately 0.06 a.u. (or 5%) too low. It is therefore clear that approaches that take account of dynamic correlation are required for obtaining reliable results for the quadrupole moment of N<sub>2</sub>. Moreover, although the situation is greatly improved by performing calculations at the MR-CI level, it also does not yield a quantitatively correct quadrupole moment. In particular, when compared with results obtained from the size-extensive modified MR-AQCC and MR-ACPF methods, for the larger basis sets the MR-CI values are about 0.003–0.007 a.u. (or 0.3%–0.6%) too low, and the discrepancy increases with the basis set size. In contrast, the differences between results obtained using the two size-extensive modified methods MR-AQCC and MR-ACPF are less than 0.002 a.u. (~0.15%).

Our examination of the basis set convergence focuses mainly on the hierarchy of calculations performed using the MR-AQCC and MR-ACPF models. As seen from Table I, for the pVXZ series of basis sets, the change in  $\Theta_e$  on increasing the “zeta order” ( $X=D, T, Q, \dots$ , etc., for double zeta, triple zeta, quadruple zeta, ..., respectively) one step at a time,  $\Theta_e^{X+1} - \Theta_e^X$ , generally decreases with increasing order. In particular, for the aug-cc-pVXZ series, when the basis set increases from the aug-cc-pV5Z to the aug-cc-pV6Z level, the changes in  $\Theta_e$  are  $\leq 0.0001$  a.u. for the MR-AQCC and MR-

ACPF methods, which indicates that use of polarized functions of order up to quintuple zeta is enough to predict highly accurate quadrupole moments for N<sub>2</sub>. However, for the cc-pVXZ series, the rate of convergence with basis set size is much slower than that for the aug-cc-pVXZ series, and this omission of augmented functions gives rise to significant discrepancies among the values of  $\Theta_e$  calculated at various orders. This occurs because the fact that the electric quadrupole moment operator is quadratic in the electronic coordinates makes it important to include diffuse functions in the basis set.

Additional questions which must also be asked are how many diffuse function are needed, and what is an estimate of the precision for a particular method? Additional calculations using the larger diffuse function basis sets of the taug-cc-pVXZ series were used to examine this aspect of convergence. As shown in Table I, for both the MR-AQCC and MR-ACPF methods, the differences between the results obtained with the doubly (daug-cc-pVXZ) and triply (taug-cc-pVXZ) augmented basis sets decrease systematically from 0.0020 to 0.0001 a.u. on proceeding from the double-zeta to the quintuple-zeta level. It is therefore clear that as the zeta order “X” increases, the effect of diffuse basis functions beyond the doubly augmented level becomes negligible. The valence basis set limit result can therefore be obtained as the common value towards which the daug-cc-pVXZ and taug-cc-pVXZ series converge, which Table I shows to be -1.1270 and -1.1244 a.u. for the MR-AQCC and MR-ACPF methods, respectively. Comparing these values with the aug-

TABLE III. Calculated values of  $(d\Theta/dR)_e$  (in a.u.) for  $N_2$  at the experimental equilibrium distance  $R_e=2.074\ 32$  a.u.

Method	X	Basis set						
		pVXZ				aug-cc-pCVXZ		
		cc	aug-cc	daug-cc	taug-cc	Contracted	Uncontracted	Uncontracted DK
HF	D	0.9746(6)	1.4866(14)	1.5385(3)	1.5368(2)	1.4806(15)		
	T	1.2846(10)	1.4390(14)	1.4390(14)	1.4401(10)	1.4288(12)		
	Q	1.3609(10)	1.4295(10)	1.4271(10)	1.4270(10)	1.4298(10)		
	5	1.3958(9)	1.4277(9)	1.4266(10)	1.4274(12)	1.4276(9)		
	6	1.4064(10)	1.4263(9)					
CASSCF	D	0.6872(6)	1.0491(9)	1.0922(8)	1.0903(3)	1.0406(11)	1.0410(4)	1.0439(4)
	T	0.9071(6)	0.9974(9)	0.9943(10)	0.9944(7)	0.9879(8)	0.9883(14)	0.9911(14)
	Q	0.9461(6)	0.9839(6)	0.9814(6)	0.9811(6)	0.9840(6)	0.9840(6)	0.9869(6)
	5	0.9629(5)	0.9813(6)	0.9803(6)	0.9810(7)	0.9812(6)	0.9810(6)	0.9839(6)
	6	0.9674(6)	0.9801(6)					
MR-CI	D	0.6963(6)	1.0308(9)	1.0775(8)	1.0759(3)	1.0228(12)	1.0235(4)	1.0263(4)
	T	0.8903(6)	0.9926(9)	0.9898(10)	0.9898(6)	0.9797(9)	0.9809(15)	0.9835(14)
	Q	0.9346(6)	0.9817(6)	0.9789(6)	0.9787(6)	0.9753(6)	0.9754(6)	0.9781(6)
	5	0.9572(6)	0.9798(6)	0.9791(6)	0.9788(6)	0.9728(6)	0.9727(6)	0.9754(6)
	6	0.9639(6)	0.9791(6)					
MR-AQCC	D	0.6946(6)	1.0216(8)	1.0693(8)	1.0680(3)	1.0079(12)	1.0081(4)	1.0110(4)
	T	0.8819(7)	0.9842(10)	0.9818(9)	0.9818(6)	0.9657(9)	0.9664(14)	0.9691(15)
	Q	0.9250(6)	0.9734(6)	0.9706(6)	0.9704(6)	0.9606(6)	0.9605(6)	0.9634(6)
	5	0.9475(6)	0.9716(6)	0.9707(6)	0.9705(6)	0.9578(6)	0.9577(6)	<b>0.9604(6)</b>
	6	0.9543(6)	0.9707(6)					
MR-ACPF	D	0.6939(7)	1.0182(8)	1.0665(8)	1.0651(3)	1.0039(11)	1.0037(5)	1.0066(5)
	T	0.8793(4)	0.9809(10)	0.9784(10)	0.9786(6)	0.9613(9)	0.9618(14)	0.9647(15)
	Q	0.9212(9)	0.9699(7)	0.9670(7)	0.9671(6)	0.9558(6)	0.9557(6)	0.9586(6)
	5	0.9440(4)	0.9680(6)	0.9673(6)	0.9671(6)	0.9528(6)	0.9527(6)	0.9556(5)
	6	0.9503(10)	0.9673(7)					

cc-pVXZ results of 1.1233 and 1.1259 a.u. for MR-AQCC and MR-ACPF, respectively, we estimate that the effect of diffuse basis functions beyond the aug-cc-pVXZ level is to be  $\leq 0.0011$  a.u. for both the MR-AQCC and MR-ACPF methods.

To investigate the effect of core correlation, the quadrupole moment was calculated using the series of core-valence basis sets aug-cc-pCVXZ with  $X=D-5$ . As shown in Table I, the difference between the results obtained at the aug-cc-pCVXZ (all electrons correlated, third-last column of Table I) and the aug-cc-pVXZ (only valence electrons correlated) levels are  $-0.0013(D)$ ,  $0.0007(T)$ ,  $-0.0042(Q)$ , and  $-0.0052(5)$  a.u. for the MR-AQCC models, and are  $-0.0015(D)$ ,  $0.0002(T)$ ,  $-0.0046(Q)$ , and  $-0.0055(5)$  a.u. for MR-ACPF models, respectively. For the larger quadruple- and quintuple-zeta basis sets, the results tend to be stable, so we conclude that the basis set aug-cc-pCV5Z does define a well converged set of results.

Scalar relativistic effects were investigated using the Douglas-Kroll (DK) one-electron Hamiltonian.<sup>22</sup> Uncontracted aug-cc-pCVXZ basis sets with  $X$  ranging from  $D$  (2) to 5 and all electrons correlated were employed in these tests, which yielded the results in the last two columns of Table I. The relativistic effect is essentially constant over the various basis sets and models, ranging from 0.0037 to 0.0039 a.u.,

and these values are in excellent agreement with those obtained by Halkier *et al.* at the CCSD level (0.0036–0.0038 a.u.).<sup>23</sup>

The results presented above show that the hierarchies of MR-AQCC and MR-ACPF models, both of which are size extensive and take account of dynamic correlation effects, always gave more consistent results than the other models. However, there still exist small absolute differences between the results yielded by these two approaches. As an independent test of them, Table II compares experimental vibrational energies  $[G_v - G_0]$  and inertial rotational constants  $B_v$  with values computed from potential energy curves calculated by these two methods. These calculations were performed by applying program LEVEL (Ref. 24) to potential energy curves calculated on a grid of 155 radial points. The results in columns 3 and 4 of Table II show that on the interval for which experimental data are available,  $v=0-19$ , which comprises the lower half of the potential well, the vibrational level spacings of the potential obtained at the MR-AQCC/aug-cc-pCV5Z (uncontracted) level with DK scalar relativistic correction are always slightly too high, while those generated from the analogous MR-ACPF potential were slightly too low. However, the disagreement with experiment for both the calculated vibrational energies and the inertial rotational constants are clearly distinctly smaller for the potential obtained



using the MR-AQCC approach. Furthermore, differences with experiment for the equilibrium bond length and dissociation energy of the potential calculated by the MR-AQCC approach are also smaller than those for the MR-ACPF potential. We therefore conclude that the MR-AQCC/aug-cc-pCV5Z (uncontracted) method with DK scalar relativistic corrections is the most reliable of the methods considered here, and hence that the value of the equilibrium quadrupole moment obtained in this way (bold font in the last column of Table I) is our best estimate of this quantity. At the same time, we may consider the difference of 0.0022 a.u. between the quintuple-zeta results obtained using these two methods as a possible measure of the uncertainty. Combining it with our estimated uncertainties due to a possible incomplete representation of diffuse functions ( $\pm 0.0011$  a.u.) and to neglect a higher polarized function ( $\pm 0.0001$  a.u.), we obtain a final equilibrium value of  $\Theta_e = -1.1273(\pm 0.0034)$  a.u. or  $5.058(\pm 0.015) \times 10^{-40}$  C m<sup>2</sup>. Our uncertainty in this quantity is significantly smaller than that in the recent experimental value of  $(4.65 \pm 0.08) \times 10^{-40}$  C m<sup>2</sup>.<sup>25</sup>

Our calculated values of the radial first derivative of the molecular quadrupole moment of N<sub>2</sub> at various theory of levels are given in Table III. The SCF results are clearly much too large, and the best CASSCF values are still slightly (*ca.* 0.01 a.u.) higher than those predicted by analogous MR-CI, MR-AQCC, and MR-ACPF calculations. The effects of polarized and diffuse functions show a good convergence there too. Based on the value calculated at the MR-AQCC/aug-cc-pCV5Z (uncontracted) level with core and scalar relativistic corrections, adding estimated uncertainties associated with possibly incomplete diffuse functions ( $\pm 0.0011$  a.u.) and with neglect of higher polarized functions ( $\pm 0.0009$  a.u.) with those associated with the difference between the MR-AQCC and MR-ACPF methods and with the fit to points to determine the radial derivatives (numbers in parentheses in Table III), our final recommended value of the radial first derivative of the quadrupole moment at the equilibrium separation is  $(d\Theta/dR)_e = 0.9604(\pm 0.0074)$  a.u.

Our final recommended distance-dependent quadrupole moment for N<sub>2</sub> was calculated using the uncontracted aug-cc-pCV5Z basis set with core correlation corrections, plus a scalar relativistic correction obtained using the Douglas-Kroll relativistic one-electron integrals. Values were generated at 155 radial distances with a range of  $(0.8-12.0)a_0$ , and a particularly dense grid of point in the region of  $(1.6-2.6)a_0$  governing the fundamental vibrational band. Interpolation over this grid yields the radial quadrupole moment function shown in Fig. 1. Also shown there are  $\Theta(R)$  functions computed at lower levels of theory. The full listing of calculated  $\Theta(R)$  values is presented in Table IV. As is seen in Fig. 1, the overall topography of the quadrupole moment functions obtained at different levels of theory is qualitatively the same. A steep near-linear behavior near  $R_e$  is followed by a dip to a local minimum near  $4.1a_0$  before approaching an asymptotic value of zero (this limit is zero because N<sub>2</sub> dissociates to *S*-state atoms). These results are consistent with the calculations which Lawson and Harrison performed at the MRCI/aug-cc-pVQZ level.<sup>7</sup> The differences

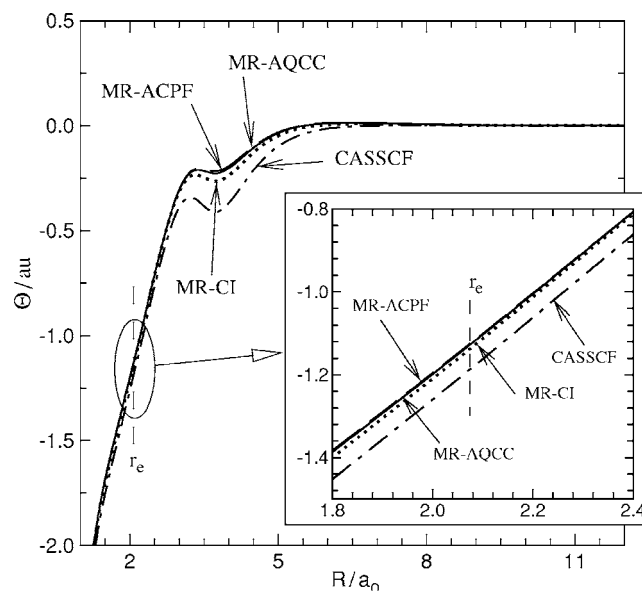


FIG. 1. Distance-dependent quadrupole moment for N<sub>2</sub> calculated at various theory of levels using an uncontracted aug-cc-pCV5Z basis set with core and scalar relativistic corrections.

between results obtained with and without the inclusion of the dynamic correlation and size-extensive modifications are clearly evident in Fig. 1.

Earlier calculations of the quadrupole moments of N<sub>2</sub>,<sup>26-34</sup> most obtained at only the SCF level, were reviewed Lawson and Harrison.<sup>7</sup> Our calculations indicate that dynamical correlation contributes approximately 0.2 a.u. (or 20% of the total) to its equilibrium value. Although Maroulis and Thakkar calculated  $\Theta(R)$  at the SDQ-MPPT(4)/6s4p3d1f level<sup>34</sup> and Piecuch *et al.* at the CCSD/54p2d level,<sup>32</sup> the basis sets that they used were too small to yield accurate values. From the preceding discussion, we know that polarized functions up to quintuple-zeta are required to yield convergence, and that diffuse function have a  $\pm 0.0011$  a.u. effect, even using a quintuple-zeta basis set. Lawson and Harrison's calculation were performed at the MRCI and CASSCF+1+2 levels;<sup>7</sup> however, they did not include size-extensive modifications. The comparisons in Table I indicate that the differences between the quadrupole moments obtained using the two size-extensive modified methods MR-AQCC and MR-ACPF are about 0.002 a.u. ( $\sim 0.15\%$ ).

A recent paper by Maroulis reported values of the quadrupole moment of N<sub>2</sub> and its distance dependence calculated using the CCSD(T) method.<sup>21</sup> However, while the value of  $\Theta_e = -1.1258$  a.u. he obtained using a large basis set ([10s7p6d4f]) is in very good agreement (within 0.13% of) with our recommended value of  $-1.1273(\pm 0.0025)$  a.u., the  $R$  dependence he reported was based on calculations performed on a small radial grid using a smaller basis set, and his value of  $(d\Theta/dR)_e = 1.0165$  a.u. is 6% larger than that associated with the present recommended value. In slightly earlier work, Halkier *et al.*<sup>23</sup> obtained a value of  $\Theta_e = -1.112(\pm 0.007)$  a.u. using the CCSD(T) method with the inclusion of small relativity corrections and correlation contributions beyond the CCSD(T) limit. However, both of these

TABLE IV. Calculated values of  $\Theta(R)$  obtained at the MR-AQCC level using an uncontracted aug-cc-pCV5Z basis set with core and scalar relativistic corrections.

$R/a_0$	$\Theta/\text{a.u.}$	$R/a_0$	$\Theta/\text{a.u.}$	$R/a_0$	$\Theta/\text{a.u.}$	$R/a_0$	$\Theta/\text{a.u.}$
0.8	-5.042 277 90	2.20	-1.005 149 39	4.5	-0.105 642 20	8.4	0.004 688 19
0.9	-3.281 783 63	2.22	-0.985 477 18	4.6	-0.088 123 31	8.5	0.004 372 96
1.0	-2.661 402 90	2.24	-0.965 752 90	4.7	-0.072 261 02	8.6	0.004 073 85
1.1	-2.330 167 44	2.26	-0.945 982 74	4.8	-0.058 156 12	8.7	0.003 790 34
1.2	-2.107 187 70	2.28	-0.926 173 73	4.9	-0.045 773 89	8.8	0.003 521 86
1.3	-1.938 709 03	2.30	-0.906 333 44	5.0	-0.035 029 41	8.9	0.003 268 15
1.4	-1.801 922 84	2.32	-0.886 471 79	5.1	-0.025 802 37	9.0	0.003 028 39
1.5	-1.684 648 19	2.34	-0.866 597 55	5.2	-0.017 959 70	9.1	0.002 802 40
1.60	-1.579 382 41	2.36	-0.846 721 05	5.3	-0.011 366 35	9.2	0.002 589 85
1.62	-1.559 297 71	2.38	-0.826 853 55	5.4	-0.005 884 33	9.3	0.002 390 48
1.64	-1.539 456 05	2.40	-0.807 007 03	5.5	-0.001 409 19	9.4	0.002 204 11
1.66	-1.519 827 89	2.42	-0.787 194 28	5.6	0.002 243 94	9.5	0.002 030 82
1.68	-1.500 385 60	2.44	-0.767 428 79	5.7	0.005 155 64	9.6	0.001 865 68
1.70	-1.481 103 50	2.46	-0.747 724 76	5.8	0.007 423 20	9.7	0.001 717 66
1.72	-1.461 957 60	2.48	-0.728 096 59	5.9	0.009 160 97	9.8	0.001 581 84
1.74	-1.442 925 61	2.50	-0.708 561 80	6.0	0.010 421 08	9.9	0.001 457 63
1.76	-1.423 986 81	2.52	-0.689 134 47	6.1	0.011 331 87	10.0	0.001 344 55
1.78	-1.405 121 91	2.54	-0.669 832 14	6.2	0.011 925 93	10.1	0.001 242 04
1.80	-1.386 313 12	2.56	-0.650 672 15	6.3	0.012 266 10	10.2	0.001 149 49
1.82	-1.367 543 97	2.58	-0.631 672 43	6.4	0.012 396 50	10.3	0.001 066 26
1.84	-1.348 799 27	2.60	-0.612 851 55	6.5	0.012 358 99	10.4	0.000 991 63
1.86	-1.330 065 16	2.7	-0.523 103 60	6.6	0.012 188 37	10.5	0.000 924 87
1.88	-1.311 321 74	2.8	-0.438 825 15	6.7	0.011 896 79	10.6	0.000 865 21
1.90	-1.292 571 89	2.9	-0.365 609 00	6.8	0.011 545 06	10.7	0.000 811 88
1.92	-1.273 798 08	3.0	-0.304 980 97	6.9	0.011 137 96	10.8	0.000 764 19
1.94	-1.254 991 07	3.1	-0.259 019 74	7.0	0.010 692 48	10.9	0.000 721 44
1.96	-1.236 142 70	3.2	-0.228 833 94	7.1	0.010 224 10	11.0	0.000 682 98
1.98	-1.217 245 85	3.3	-0.213 810 26	7.2	0.009 740 25	11.1	0.000 648 20
2.00	-1.198 294 44	3.4	-0.211 191 32	7.3	0.009 249 76	11.2	0.000 616 63
2.02	-1.179 283 43	3.5	-0.216 187 69	7.4	0.008 747 02	11.3	0.000 587 73
2.04	-1.160 208 37	3.6	-0.223 069 35	7.5	0.008 267 77	11.4	0.000 561 13
2.06	-1.141 066 87	3.7	-0.226 956 79	7.6	0.007 824 26	11.5	0.000 536 49
2.074 32	-1.127 319 30	3.8	-0.224 992 92	7.7	0.007 373 41	11.6	0.000 513 46
2.08	-1.121 856 47	3.9	-0.216 588 07	7.8	0.006 941 38	11.7	0.000 491 85
2.10	-1.102 576 07	4.0	-0.202 679 97	7.9	0.006 521 42	11.8	0.000 471 41
2.12	-1.083 225 44	4.1	-0.184 997 96	8.0	0.006 121 38	11.9	0.000 452 00
2.14	-1.063 805 32	4.2	-0.165 215 55	8.1	0.005 736 88	12.0	0.000 433 48
2.16	-1.044 317 42	4.3	-0.144 747 36	8.2	0.005 370 02	12.1	0.000 415 76
2.18	-1.024 764 28	4.4	-0.124 658 70	8.3	0.005 021 42		

relatively recent calculations agree with the present conclusion that the most recent experimental value<sup>25</sup> of  $\Theta_e = -4.65(\pm 0.08) \times 10^{-40} \text{ C m}^2$  is  $\sim 8\%$  too high (too small in magnitude).

Values of the static average dipole polarizability  $\bar{\alpha}$  and polarizability anisotropy  $\Delta\alpha$  of  $\text{N}_2$  at the experimental equilibrium internuclear separation ( $R_e = 2.074\ 32$  a.u.) were also calculated at the MR-AQCC/aug-cc-pCV5Z (uncontracted) level with core and scalar relativistic corrections. The resulting values of  $\Delta\alpha = 4.551(\pm 0.010)$  a.u. and  $\bar{\alpha} = 11.600(\pm 0.05)$  a.u. differ slightly (by 1.2% and 1.5%) from values which Maroulis<sup>21</sup> recently obtained [4.6074 and 11.7709] from calculations at the CCSD(T)/[10s7p6d4f] level. Comparisons analogous to those shown in Tables I and II indicate that these differences are not due to Maroulis' neglect of core correlation and relativistic effects. A CCSD(T) calculation performed using the same large basis

[22s20p16d12f8g4h] used for our recommended MR-AQCC results yields  $\Delta\alpha = 4.5824$  a.u. and  $\bar{\alpha} = 11.7412$  a.u., which show that basis size accounts for only a fraction of the difference. Thus, it appears that the remaining differences with the large-basis CCSD(T) results of 0.7% in  $\Delta\alpha$  and 1.2% in  $\bar{\alpha}$  are due to the different methodologies, CCSD(T) versus MR-AQCC. However, the analogous difference for the equilibrium quadrupole moment  $\Theta_e$  is an order of magnitude smaller, so the effect of these differences in methodology on our quadrupole moment results is less than our estimated uncertainty.

### III. CALCULATION OF QUADRUPOLE AND POLARIZABILITY MATRIX ELEMENTS AND OF QUADRUPOLE LINE INTENSITIES

Accurate values of  $J$ -dependent quadrupole matrix elements  $\langle v', J' | \Theta(r) | v'', J'' \rangle$  for ground-state  $\text{N}_2$  may be readily

TABLE V. Quadrupole transition energies and intensity factors for the fundamental band of N<sub>2</sub>, calculated using the potential energy function of Ref. 8 and quadrupole moment functions calculated at the MR-AQCC level using an uncontracted aug-cc-pCV5Z basis set with core and scalar relativistic corrections.

$J$	Transition energies			$ \langle v', J'   \Theta(R)   v'', J'' \rangle ^2 / 10^{-3}$		
	$\nu_S(J)$	$\nu_Q(J)$	$\nu_O(J)$	$S(J)$	$Q(J)$	$O(J)$
0	2341.74			3.4427		
1	2349.60	2329.88		3.4687	3.4040	
2	2357.42	2329.81	2317.97	3.4949	3.4041	3.3656
3	2365.20	2329.70	2309.98	3.5213	3.4043	3.3402
4	2372.95	2329.56	2301.96	3.5478	3.4046	3.3150
5	2380.66	2329.39	2293.89	3.5745	3.4049	3.2899
6	2388.33	2329.18	2285.80	3.6013	3.4053	3.2650
7	2395.97	2328.94	2277.67	3.6283	3.4058	3.2403
8	2403.57	2328.66	2269.51	3.6555	3.4063	3.2157
9	2411.13	2328.35	2261.32	3.6828	3.4068	3.1913
10	2418.65	2328.00	2253.10	3.7103	3.4075	3.1670
11	2426.14	2327.62	2244.84	3.7380	3.4082	3.1429
12	2433.59	2327.20	2236.55	3.7658	3.4090	3.1189
13	2441.00	2326.75	2228.23	3.7938	3.4098	3.0951
14	2448.37	2326.26	2219.88	3.8219	3.4107	3.0715
15	2455.70	2325.74	2211.49	3.8502	3.4117	3.0480
16	2462.99	2325.19	2203.08	3.8787	3.4127	3.0247
17	2470.25	2324.59	2194.64	3.9074	3.4138	3.0015
18	2477.46	2323.97	2186.16	3.9362	3.4150	2.9785
19	2484.63	2323.31	2177.66	3.9652	3.4162	2.9556
20	2491.77	2322.61	2169.12	3.9943	3.4175	2.9329
21	2498.86	2321.88	2160.56	4.0236	3.4189	2.9104
22	2505.91	2321.12	2151.97	4.0531	3.4203	2.8880
23	2512.92	2320.32	2143.34	4.0828	3.4218	2.8658
24	2519.89	2319.49	2134.69	4.1126	3.4234	2.8437
25	2526.81	2318.62	2126.02	4.1426	3.4250	2.8217
26	2533.70	2317.70	2117.31	4.1727	3.4267	2.8000
27	2540.54	2316.77	2108.57	4.2030	3.4285	2.7783
28	2547.34	2315.80	2099.81	4.2335	3.4303	2.7569
29	2554.10	2314.79	2091.02	4.2642	3.4322	2.7356
30	2560.81	2313.75	2082.21	4.2950	3.4342	2.7144
31	2567.48	2312.67	2073.36	4.3260	3.4362	2.6934
32	2574.11	2311.56	2064.49	4.3572	3.4383	2.6725
33	2580.69	2310.41	2055.60	4.3886	3.4405	2.6518
34	2587.22	2309.23	2046.68	4.4201	3.4427	2.6313
35	2593.72	2308.01	2037.73	4.4518	3.4450	2.6109
36	2600.16	2306.76	2028.76	4.4836	3.4474	2.5906
37	2606.57	2305.47	2019.76	4.5157	3.4498	2.5705
38	2612.92	2304.15	2010.74	4.5479	3.4524	2.5505
39	2619.24	2302.79	2001.69	4.5803	3.4549	2.5307
40	2625.50	2301.40	1992.62	4.6128	3.4576	2.5111

obtained by combining the quadrupole moment function of Table IV with exact (numerical) radial wave functions generated from the empirical potential energy function of Ref. 8. Such calculations may be performed using a standard Franck-Condon overlap code such as LEVEL.<sup>24</sup> Although the best *ab initio* potential function obtained in the present work has spectroscopic properties in fairly good agreement with experiment (see Table II), orders of magnitude better agreement is obtained with that empirical potential.<sup>8</sup> Tests showed that simple cubic-spline interpolation over the grid of calculated  $\Theta(R)$  values sufficed to yield calculated fundamental-band quadrupole matrix elements converged to better than  $10^{-6}$  a.u. An illustrative sample of  $J$ -dependent quadrupole

intensity factors  $|\langle v', J' | \Theta(r) | v'', J'' \rangle|^2$  for the fundamental band of N<sub>2</sub> is presented and listed in Table V, and a more extensive compilation is available as supplementary EPAPS files.<sup>35</sup>

The upper segment of Fig. 2 shows the  $J$  dependence of our calculated intensity factors  $|\langle v', J' | \Theta(r) | v'', J'' \rangle|^2$  for the  $O$ ,  $Q$ , and  $S$  branches of the fundamental band of N<sub>2</sub>. The solid round points were obtained with our recommended MR-AQCC quadrupole moment function and the open triangular points with the analogous MR-ACPF function. For comparison, the solid square points show intensity factors calculated using the matrix element  $\langle 0, 0 | \Theta(R) | 1, 0 \rangle$

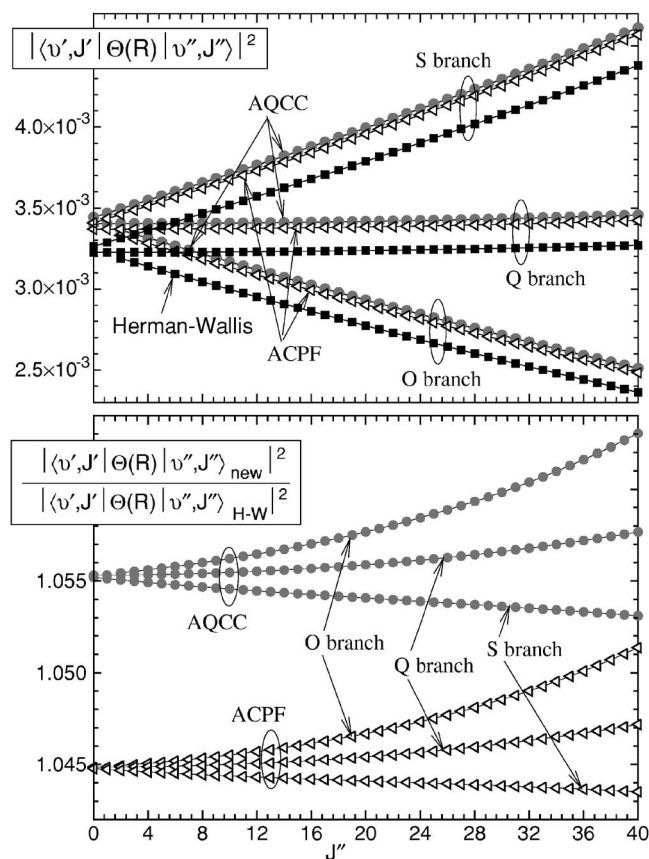


FIG. 2. Upper: fundamental-band quadrupole intensity factors for  $N_2$  based on quadrupole moment functions calculated at the MR-AQCC (round points) and MR-ACPF (triangular points) levels using an uncontracted aug-cc-pCV5Z basis set with core and scalar relativistic corrections; square (“Herman-Wallis”) points obtained as described Ref. 4. Lower: ratio of *ab initio* intensity factors to Herman-Wallis (H-W) values of Ref. 4.

$=5.67938(\pm 0.24) \times 10^{-2}$  a.u. adopted by Goldman *et al.*<sup>4</sup> and the extended Herman-Wallis  $F$  factor of their Eq. (10). A more sensitive examination of the  $J$  dependence of their results is presented in the lower segment of Fig. 2, which shows the presence of small, but systematic errors in the  $J$  dependence predicted by the Herman-Wallis  $F$  factors of Ref. 4. The  $\sim 1\%$  difference between the magnitudes of the MR-AQCC and MR-ACPF intensity factors is a measure of the uncertainty in our estimate of the quadrupole radial derivative. However, as discussed earlier, we prefer the AQCC predictions.

Finally, Fig. 3 illustrates the dependence of the  $\Delta v=1$  and  $\Delta v=2$  vibrational intensities on  $v''$ . It is interesting to see the 20-fold increase in the predicted vibrational band intensities over this vibrational interval.

#### IV. DISCUSSION AND CONCLUSIONS

The present work presents an *ab initio* quadrupole moment function calculated over a wide range of internuclear distance on a fairly dense radial mesh. Detailed convergence tests suggest that these results have an estimated absolute accuracy of  $\pm 0.0034$  a.u. or 0.3% of  $\Theta_e$ . As noted above, our equilibrium value of the quadrupole moment,  $5.058 \times 10^{-40}$  C m<sup>2</sup>, is significantly larger than the most recent experimental value of  $-4.65(\pm 0.08) \times 10^{-40}$  C m<sup>2</sup>, reported by

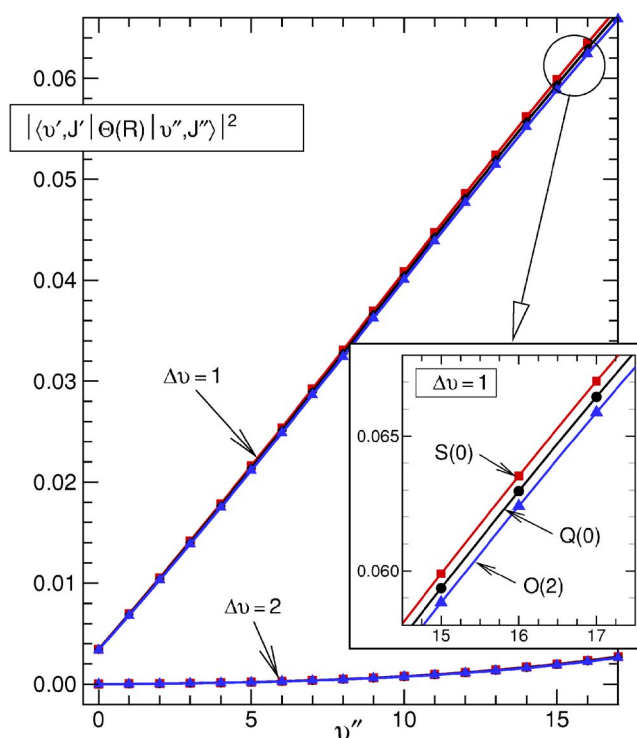


FIG. 3. Vibrational dependence of calculated  $N_2$  intensity factors  $|\langle v', J' | \Theta(R) | v'', J'' \rangle|^2$ , in a.u.

Graham *et al.*<sup>25</sup> However, the latter value was based on a room temperature value of  $-5.25(\pm 0.08) \times 10^{-40}$  C m<sup>2</sup> which was corrected to 0 K using a correction term based on an estimate of a hyperpolarizability factor which was taken as the average of two *ab initio* values which differed by a factor of 4.4.<sup>34,36</sup> If the smaller of those theoretical values is used, the correction would yield a value of  $-5.03(\pm 0.08) \times 10^{-40}$  C m<sup>2</sup>, in excellent agreement with the present result. However, another way to perform this comparison is to replace our equilibrium value of  $\Theta_e$  by a thermal average of the expectation values  $\bar{\Theta}_{v,J} = \langle v, J | \Theta(R) | v, J \rangle$ . The resulting average values are  $\bar{\Theta}(T) = (-5.025$  and  $-5.022) \times 10^{-40}$  C m<sup>2</sup> for  $T=0$  and 298 K, respectively. This calculation indicates that thermal averaging actually has little effect on the overall quadrupole moment. Thus, our final conclusion is that the best existing experimental measurement of  $\Theta_e$ , corrected for the vibrational and thermal averagings as reported above, is actually  $-5.29(\pm 0.08) \times 10^{-40}$  C m<sup>2</sup>, which is slightly too high, though the 4.5% difference is only slightly outside the mutual uncertainties of 1.5% and 1%.

The present results also suggest (lower segment of Fig. 2) that the previous best semiempirical estimates<sup>4</sup> of the IR transition intensities of  $N_2$  are ca. 5% too small. Thus, the quadrupole intensity factors implied by the present work suggests that work using  $N_2$  infrared intensities to determine atmospheric concentration profiles should be reassessed.

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- <sup>35</sup>See EPAPS Document No. E-JCPSA6-126-016721 for ASCII files containing an extended list of calculated transition energies and quadrupole matrix elements for all transitions with  $J=0-50$ ,  $\Delta v=0-3$ , and  $v'=0-3$ . This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
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