

A coupled cluster study of the spectroscopic properties and electric dipole moment functions of nitrous sulfide

Youngshang Pak and R. Claude Woods

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Kirk A. Peterson

Department of Chemistry, Washington State University, and the Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, Richland, Washington 99352

(Received 27 September 1995; accepted 22 January 1996)

Three-dimensional near-equilibrium potential energy surfaces and dipole moment functions have been calculated for the ground state of nitrous sulfide (NNS), using a large basis set and the coupled cluster method with single and double substitutions, augmented by a perturbative estimate of triple excitations [CCSD(T)]. The CCSD(T) equilibrium bond lengths with a correlation consistent polarized valence quadruple zeta (cc-pVQZ) basis set are $r_e(\text{NN})=1.1284 \text{ \AA}$ and $R_e(\text{NS})=1.5904 \text{ \AA}$, which have been corrected to 1.126 and 1.581 \AA , respectively, based on the results of the corresponding calculations on the NN and NS diatomics. Rotational–vibrational energy levels and the corresponding infrared intensities for NNS have been determined using variational methods with the CCSD(T)/cc-pVQZ potential energy and dipole moment functions. The calculated band origins (cm^{-1}) ν_1 , ν_2 , and ν_3 and their intensities (km/mol) at the CCSD(T)/cc-pVQZ level are 740.7/38.6, 463.1/0.01, and 2061.4/385.8, respectively. A complete set of second-order spectroscopic constants have been obtained from the *ab initio* potential energy surface using both the standard perturbation theory formulas and the variationally determined rovibrational energies. Comparison of the theoretical vibration–rotation interaction constants (α_i) with those obtained from the published high resolution Fourier transform infrared (FTIR) spectra clearly demonstrate that the rotational quantum number (J) assignments must be revised in all the observed hot bands. A new set of spectroscopic constants for NNS, derived from a reanalysis of the published FTIR frequencies, is presented. These are in excellent agreement with our CCSD(T) predictions. Values of the quadrupole coupling constants at each nucleus are predicted using multireference configuration interaction (MRCI) with the same cc-pVQZ basis. © 1996 American Institute of Physics. [S0021-9606(96)02816-7]

I. INTRODUCTION

The nitrous sulfide molecule (NNS) was first observed by infrared (IR) spectroscopy and mass spectrometry as a decomposition product of the flash vacuum pyrolysis (FVP) of 5-phenyl-1,2,3,4-thiaziazole.¹ A high resolution infrared spectroscopic study of NNS has been carried out by Brown *et al.*² using the FVP production scheme. They determined the ν_3 fundamental frequency (NN stretching) to be 2047.59 cm^{-1} and derived the r_0 structure of NNS, $r_0(\text{NN})=1.1388 \text{ \AA}$ and $R_0(\text{NS})=1.5775 \text{ \AA}$, on the basis of B_0 constants from the spectroscopic studies on the normal and NN³⁴S isotopes. The stretching fundamental frequencies ν_1 and ν_3 in an Ar matrix were observed to be 752 and 2039 cm^{-1} by Kambouris *et al.*³ Also the isotopic shifts of the NN stretching fundamental were investigated by Hassanzadeh and Andrews⁴ in infrared spectra of NNS isotopomers in an Ar matrix. Several correlated *ab initio* calculations on NNS in the ground electronic state ($^1\Sigma^+$)^{5–7} have been carried out recently using the complete active space self-consistent-field (CASSCF) method, the configuration interaction method with single and double substitutions (CISD), the coupled cluster method with single and double substitutions (CCSD), and CCSD augmented by the perturbative treatment of triple excitations [CCSD(T)].⁸ Davy and Schaefer⁵ investigated possible structural isomers of NNS using the CISD and

CCSD levels of *ab initio* theory, showing that linear NNS is the most stable form, and Collins *et al.*⁶ carried out CCSD(T) calculations for the ground state of NNS with larger basis sets, resolving several important discrepancies between experiment and theory. The *ab initio* studies in Refs. 5 and 6, however, were mainly limited to predictions of the equilibrium structure or harmonic frequencies and intensities using analytic gradient methods. In an attempt to make more direct comparisons with experimentally obtained vibrational frequencies, Wong and Bacskay⁷ have also performed a CCSD(T) study of the near equilibrium potential energy surface of NNS in its ground electronic state, yielding vibrational band origins up to 4100 cm^{-1} , variationally determined, as well as anharmonic force constants.

The present work also involves a large basis set CCSD(T) investigation of the near equilibrium region of the NNS ground state potential energy surface, but it is extended in several respects in comparison to the studies described in Refs. 6 and 7. The largest basis set used here is at the quadruple zeta level rather than triple zeta level used in the earlier work^{6,7} and includes polarization functions through g type. A complete electric dipole moment function (EDMF) has been obtained in addition to the potential energy function (PEF). The variational programs of Tennyson and co-workers^{9,10} have been employed to obtain $J=0–2$ energy

levels in all vibrational states up to 4900 cm^{-1} , along with the corresponding infrared band intensities, from the CCSD(T) PEF and EDMF for NNS. A full set of second-order spectroscopic constants (vibration–rotation interaction, anharmonicity, etc.) are derived from the *ab initio* PEF, using both perturbation theory formulas and in some cases the variational energy levels. The extensive high resolution study of the NN stretching region (ν_3) of NNS by Fourier transform infrared (FTIR) spectroscopy² included many hot band lines. Analyses of 5 of these hot bands was presented in Ref. 2, leading among other things to a complete set of vibration–rotation interaction constants (α_1 , α_2 , and α_3). Of these, α_3 , which is derived from fundamental band data, is in excellent agreement with our CCSD(T) value, but α_1 and α_2 , which come from the hot band analyses, are in serious disagreement. Furthermore the FTIR results for α_1 and α_2 are inconsistent with the pattern exhibited by related molecules, e.g., OCS and NCS⁻, whereas the α_1 and α_2 values produced at all levels of theory up to our highest, by either perturbation methods or variational methods, fall within the typical expected range for this isoelectronic sequence. We have traced the discrepancies to the assignment of the J quantum numbers in the hot bands. We present a reanalysis based on a revised J numbering in all five hot bands and a new set of FTIR spectroscopic constants for NNS. These new experimental values are in excellent agreement with our CCSD(T) results. We have attempted also to estimate the equilibrium structure of NNS by combining the FTIR B_0 's and our theoretical α_i 's for normal isotopic NNS and NN³⁴S. There remain some discrepancies between the resultant r_e 's and those from our CCSD(T) calculations. When the latter are corrected by reference to results for the diatomic NN and NS molecules, the NS distance prediction is substantially improved, but the agreement for the NN distance is slightly degraded.

II. DETAILS OF THE CALCULATIONS

The correlation consistent polarized valence quadruple zeta (cc-pVQZ) basis set, as well as the correlation consistent polarized valence triple zeta (cc-pVTZ) basis set, of Dunning¹¹ and Woon and Dunning,¹² were used in these calculations. The cc-pVTZ basis set consisted of a (10s5p2d1f) primitive set contracted to a [4s3p2d1f] for N and a (15s9p2d1f) primitive set contracted to [5s4p2d1f] for S. The cc-pVQZ basis set is designated as a (12s6p3d2f1g) primitive set contracted to a [5s4p3d2f1g] for N and a (16s11p3d2f1g) primitive set contracted to [6s5p3d2f1g] for S. The CCSD(T) calculations^{13,14} with both the cc-pVTZ and cc-pVQZ basis sets were carried out using the MOLPRO suite of *ab initio* programs,¹⁵ with only the valence electrons being correlated. A total of 54 symmetry-unique points for NNS were calculated over approximately $-0.3a_0 \leq \Delta r(\text{NN}) \leq 0.5a_0$, $-0.4a_0 \leq \Delta R(\text{NS}) \leq 0.7a_0$, and $-30^\circ \leq \Delta\theta(\angle\text{NNS}) \leq 30^\circ$ around the experimentally determined geometry.² The resulting CCSD(T) energy values were then fit to polynomials in the internal displacement coordinates:

$$V(S_1, S_2, S_3) = \sum_{ijk} (S_1)^i (S_2)^j (S_3)^k, \quad (1)$$

where S_1 , S_2 , $S_3 = \Delta r(\text{NN})$, $\Delta R(\text{NS})$, $\Delta\theta(\angle\text{NNS})$, respectively. Our CCSD(T)/cc-pVTZ calculations of the PEF overlap the previous work of Wong and Bacskay,⁷ except that our sampling region in the potential energy surface is somewhat expanded along the direction of NS stretching and that several cross terms of quintic and sextic order have been neglected in our expansion of the potential energy surface. The fitting of the potential energy surfaces and the calculations of the second-order spectroscopic constants¹⁶ were carried out using the SURFIT program.¹⁷ Electric dipole moments were also computed at each geometry sampled for the potential energy calculations, using a finite field method with field strengths of ± 0.002 a.u. Each dipole moment vector was shifted and rotated into an Eckart reference frame.^{18–20} Thus the z axis in the Eckart frame was defined as the $C_{\infty v}$ axis, to which the x axis is perpendicular, with the origin of the axes chosen as the center of mass. The dipole moments in the Eckart frame defined above were fit to quartic polynomials of the form of Eq. (1), with expansion coefficients denoted by D_{ijk}^m , where $m = z$ or x . Electric field gradients for NNS were calculated by the internally contracted multireference configuration interaction (CMRCI) method^{21–23} with the cc-pVQZ basis. In the CMRCI the reference function was obtained by selecting configurations from a full valence CASSCF calculation^{24,25} with a selection threshold of 0.01.

Using the analytical potential energy and dipole moment functions, full 3D variational calculations were carried out to obtain accurate rovibrational energy levels and dipole moment matrix elements. These calculations used the program suites of Tennyson and co-workers.^{9,10} The reader is referred to the original references for the specific details of the methods. The vibrational basis functions were constructed from products of Morse functions for the stretches, and the angular coordinate was treated using a discrete variable representation (DVR) based on associated Legendre polynomials. A total of 17 Morse functions were used for the NS stretching coordinate, while 12 functions were used for the NN stretch. For the angular coordinate, 80 DVR points were chosen (over $\theta = 0$ – 180°). After solving the effective 2D radial Hamiltonian at each DVR point, the solutions with energies lower than $15\,000\text{ cm}^{-1}$ were selected to construct the full 3D Hamiltonian matrix, which was then diagonalized to obtain the eigenvalues and eigenvectors. The sizes of the resulting matrices were generally smaller than 1000×1000 in order to converge the lowest 60–80 eigenvalues to within 0.1 – 1.0 cm^{-1} . For the calculations involving nonzero total angular momentum ($J > 0$), a two-step procedure was used, as outlined in Ref. 9.

III. SPECTROSCOPIC CONSTANTS AND POTENTIAL ENERGY FUNCTIONS

The PEFs for NNS calculated by CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ are shown in Table I, where the rms deviations of both of the fitted surfaces are less than 0.4

TABLE I. The expansion coefficients of the CCSD(T) potential energy functions for NNS (in a.u.).

i	j	k^a	CCSD(T)/cc-pVTZ	CCSD(T)/cc-pVQZ
			C_{ijk}^b	C_{ijk}^c
0	0	0	-507.048 848	-507.098 146
2	0	0	0.580 052	0.582 689
1	1	0	0.086 563	0.089 589
0	2	0	0.161 813	0.165 538
0	0	2	0.063 295	0.063 724
3	0	0	-0.772 099	-0.775 329
2	1	0	-0.042 935	-0.043 642
1	2	0	-0.012 722	-0.016 841
0	3	0	-0.206 354	-0.209 853
1	0	2	-0.057 249	-0.058 030
0	1	2	-0.069 203	-0.069 276
4	0	0	0.621 182	0.625 633
3	1	0	-0.013 131	-0.013 874
2	2	0	0.033 105	0.036 235
1	3	0	0.008 759	0.010 688
0	4	0	0.134 821	0.136 456
2	0	2	-0.007 372	-0.006 795
1	1	2	0.078 877	0.077 385
0	2	2	0.026 293	0.025 964
0	0	4	0.011 335	0.011 929
5	0	0	-0.402 547	-0.400 819
0	5	0	-0.065 954	-0.067 033
0	1	4	-0.010 074	-0.011 347
4	1	0	0.024 801	0.025 563
6	0	0	0.181 255	0.172 889
0	6	0	0.024 844	0.025 816
0	0	6	0.002 174	0.001 643

^aThe indices i , j , and k are defined in Eq. (1) of the text.

^bExpanded about $r(\text{NN})=2.138\ 110a_0$, $R(\text{NS})=3.020\ 803a_0$, $\theta=180.0^\circ$.

^cExpanded about $r(\text{NN})=2.132\ 398a_0$, $R(\text{NS})=3.005\ 359a_0$, $\theta=180.0^\circ$.

cm^{-1} . Various rotational and vibrational spectroscopic constants are obtained from both the triple zeta and quadruple zeta PEFs by second-order perturbation theory and are displayed with the bond distances in Table II. Most of the spectroscopic constants at the CCSD(T)/cc-pVQZ level were also derived from the variationally calculated rotational-vibrational energy levels, and these values are also shown in Table II, parenthetically. The column labeled FTIR (orig.) gives the published values² of several of these constants derived from the original analyses of the gas phase high resolution infrared data. In addition to the ν_3 fundamental bands for NNS and NN^{34}S the following hot bands in normal NNS were analyzed in Ref. 2: $(100)\rightarrow(101)$, $(200)\rightarrow(201)$, $(01^1e0)\rightarrow(01^1e1)$, $(01^1f0)\rightarrow(01^1f1)$, and $(02^2f0)\rightarrow(02^2f1)$. The experimental α_3 constant, which comes from the FTIR fundamental band, is in excellent agreement with the *ab initio* results, but the FTIR α_1 (7.67 MHz) and α_2 (-38.52 MHz) are not. The experimental α_1 values (in MHz) in OCS and NCS^- are 37.46 and 25.33, respectively, while the α_2 values are -10.75 and -9.50 in the same order.^{26,27} Inspection of Table II reveals that the *ab initio* predictions of these two numbers for NNS are essentially converged with respect to basis set and also that the variational calculations support the second-order perturbation theory results. The problem with α_1 and α_2 led us to reexamine the rotational quantum number assignments in the various FTIR hot bands, since

this was practically the only reasonable approach to resolving the discrepancies. The vibrational quantum number assignments of the hot bands were strongly supported by the *ab initio* results (*vide infra*) and seemed to be beyond doubt. After experimenting with various possible J assignments we found that one and only one choice produced a reasonable pattern of $B_{v_1v_2v_3}$ values and α_i 's in agreement with the theoretical results. In the three hot bands with one quantum of vibrational excitation in either the bend or NS stretch mode, m must be changed to $m-1$, while in the two bands involving $v_1=2$ or $v_2=2$ m must be shifted to $m-2$. Here m is the conventional Fortrat parabola index ($J''+1$ in the R branch and $-J''$ in the P branch). Thus in the $(200)\rightarrow(201)$ band for example the line previously assigned as $R(8)$ or $m=9$ becomes $R(6)$ or $m=7$, while the line previously thought to be $P(1)$ or $m=-1$ is now assigned as $P(3)$ or $m=-3$. The revised and published band origins and rotational and centrifugal distortion constants are given in Table III. The band origins are shifted by 0.4–0.9 cm^{-1} and the rotational constants of the hot bands by 30–65 MHz. In Table II a column labeled FTIR (rev.) gives the revised values of those spectroscopic constants affected by the reanalysis. With α_1 and α_2 taken from this column, all three of the α_i values are now in excellent agreement with the *ab initio* predictions of them, as are the anharmonicity constants X_{13} and X_{23} , which can be extracted from the band origins for the $v_1=1$ and $v_2=1$ hot bands, respectively. The pattern of B values is also very systematic in sequences of $v_1=0,1,2$ or $v_2=0,1,2$, indicating small values of the higher-order vibration rotation interaction constants (γ 's) and confirming the new assignments in all the hot bands. This improved agreement is especially evident in Table IV, which compares the FTIR rotational constants with those calculated variationally from the CCSD(T)/cc-pVQZ potential energy surface. The difference (Δ) is nearly constant at ~ 56 MHz for the revised values (*vide infra* for the exception, B_{201}), but not for the original ones. Note that now $B_e > B_0$, as would be expected. Also in regard to the new assignments it should be mentioned that the line at $2041.064\ 75\ \text{cm}^{-1}$ in the table for the $v_2=1$ hot bands (formerly $m=2$, now $m=1$) cannot belong to this band, because there is no $R(0)$ line when $l=1$. The original assignment also suffers a similar difficulty in that no $m=-1$ line would be expected in the $v_2=1$, $l=1$ bands and no $m=-2$ line ($J=2\rightarrow 1$) would be expected in a $v_2=2$, $l=2$ band. Even though the lines closest to the band gap in the ^{34}S isotope band were not assigned, the J numbering in that band is secure, because any other choice gives completely unrealistic molecular structure results.

Since the *ab initio* calculations of the vibration-rotation interaction constants now seem to be quite reliable, we have chosen to estimate B_e 's for both relevant isotopic forms of NNS from the FTIR B_0 's and the CCSD(T)/cc-pVQZ values of $\alpha_2 + (\alpha_1 + \alpha_3)/2$, where the latter quantity was derived from the variationally calculated B 's for the ground and fundamental states. This process leads to $B_e^{\text{est}}(\text{NNS}) = 6517.27$ MHz and $B_e^{\text{est}}(\text{NN}^{34}\text{S}) = 6358.60$ MHz, which in turn produce our best estimate of the equilibrium geometry of NNS.

TABLE II. Spectroscopic constants and bond distances of NNS.

Constants	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ ^a	Experiment		
			FTIR (orig.) ^b	FTIR (rev.) ^c	Solid state
$r_e(\text{NN})$ (Å)	1.1314	1.1284			
$R_e(\text{NS})$ (Å)	1.5985	1.5904			
$r_0(\text{NN})$ (Å)	1.1411	1.1379	(1.1366)	1.1388	
$R_0(\text{NS})$ (Å)	1.5968	1.5886	(1.5897)	1.5775	
B_e (MHz)	6406.38	6461.43		6469.791	6517.085
$B_e(^{34}\text{S})$	6250.10	6303.88			
B_0 (MHz)	6377.38	6432.91	(6432.65)	6488.41	
$B_0(^{34}\text{S})$	6222.05	6276.29	(6275.86)	6330.83	
α_1 (MHz)	39.71	39.43	(39.87)	7.67	39.43
α_2 (MHz)	-6.67	-6.92	(-6.67)	-38.52	-6.88
α_3 (MHz)	31.61	31.46	(31.18)	32.12	
D_e (kHz)	1.93	1.93		1.96	
q_e (MHz)	8.24	8.32	(8.54)	8.14	7.88
ω_1 (cm ⁻¹)	750.3	758.9			
ω_2 (cm ⁻¹)	464.9	468.1			
ω_3 (cm ⁻¹)	2089.8	2093.6			
ν_1 (cm ⁻¹)	731.9	740.6	(740.7)		752 ^d
ν_2 (cm ⁻¹)	459.7	463.1	(463.1)		
ν_3 (cm ⁻¹)	2057.6	2061.6	(2060.4)	2047.6	2040.2 ^e 2039 ^d
X_{11} (cm ⁻¹)	-7.49	-7.42	(-7.47)		
X_{22} (cm ⁻¹)	0.12	0.22	(0.055)		
X_{33} (cm ⁻¹)	-13.60	-13.53	(-13.61)		
X_{13} (cm ⁻¹)	3.59	3.72	(2.42)	2.21	2.63
X_{12} (cm ⁻¹)	-5.19	-5.25	(-4.97)		
X_{23} (cm ⁻¹)	-6.78	-6.75	(-6.53)	-7.39	-6.96
X_{ll} (cm ⁻¹)	0.18	0.13	(-0.061)		
G_{000} (cm ⁻¹)	1874.7	1884.3	(1883.85)		

^aThe values in parentheses are derived from variationally calculated rotational–vibrational energy levels for the CCSD(T)/cc-pVQZ potential energy function of NNS.

^bThe original FTIR results in gas phase (Ref. 2).

^cThe revised FTIR results in gas phase.

^dSolid Ar matrix infrared results from flash vacuum pyrolysis (FVP) (Ref. 3).

^eSolid Ar matrix infrared result from microwave discharge (Ref. 4).

$r_e^{\text{est.}}(\text{NN}) = 1.1307$ Å and $R_e^{\text{est.}}(\text{NS}) = 1.5782$ Å. Since the accuracy of the derived structure depends on the accuracy of the isotope shift in B_e , use of theoretical α 's for both isotomers should be a better choice than using the experimental B_e for the main isotope and an estimated B_e for the NN³⁴S species. Similarly an r_0 structure can be calculated directly from the cc-pVQZ B_0 's ($r_0^Q = 1.1366$ Å, $R_0^Q = 1.5897$ Å) and compared to the FTIR r_0 structure (Table II). (The partial r_s structure mentioned in Ref. 2 is by definition exactly the same as the r_0 structure when data are available only for two isotopomers.) The differences of the *ab initio* r_0 's from the FTIR ones should be very close to those of the *ab initio* r_e 's from the $r_e^{\text{est.}}$ values, since the same α values enter in either comparison. The cc-pVTZ value of r_e (1.1314 Å) is large relative to the $r_e^{\text{est.}}$ by only 0.0007 Å, and extension of the basis set to cc-pVQZ decreases it by 0.0030 Å, so that our highest level purely *ab initio* value of $r_e(\text{NN})$ is too short by 0.0023 Å relative to $r_e^{\text{est.}}$. The triple zeta result for R_e (1.5985) exceeds $R_e^{\text{est.}}$ by 0.0203, but going to the quadruple zeta basis decreases R_e by 0.0081 Å, in this case a substantial improvement, leaving the *ab initio* value higher by 0.0122 Å than $R_e^{\text{est.}}$. We have also attempted to improve the

theoretical estimate of the molecular structure of NNS by applying corrections to the CCSD(T)/cc-pVQZ bond lengths based on calculations on the diatomic fragments NN²⁹ and NS³⁰ at the same level of theory. The CCSD(T)/cc-pVQZ bond distances of these diatomics are $r_e(\text{NN}) = 1.0977$ Å and $r_e(\text{NS}) = 1.4940$ Å, which are longer than the corresponding experimental values³¹ by 0.0026 and 0.0096 Å. Applying these corrections to NNS gives $r_e(\text{corr.}) = 1.126$ Å and $R_e(\text{corr.}) = 1.581$ Å and $B_e^{\text{corr.}} = 6521.2$ MHz, which is within about 7 MHz of the experimental value, to some extent fortuitously, because the remaining differences between the corrected and estimated bond lengths are opposite in sign ($\Delta r = -0.0047$ Å and $\Delta R = 0.0028$ Å). Extension to a quintuple zeta basis would be expected to further decrease the two purely *ab initio* bond distances (but presumably not the corrected ones) by small amounts (~ 0.001 and ~ 0.003 Å) based on the calculations for the diatomic molecules, leaving significant errors relative to the $r_e^{\text{est.}}$ values. The unusual sensitivity of the bond lengths of NNS to the level of correlation treatment, and the difficulty of obtaining quantitative accuracy, in the sense of tending to underestimate the NN distance and overestimate the NS distance has been discussed

TABLE III. Original and revised rotational and centrifugal distortion constants for NNS from FTIR data.^a

	(000)→(001)		(100)→(101)	
	orig. (NNS) ^c	orig. (NN ³⁴ S) ^c	orig. ^c	rev. ^d
$\tilde{\nu}_0$ (cm ⁻¹)	2047.591 873(98)	2047.408 97(20)	2049.797 85(24)	2050.226 10(29)
B'' (MHz)	6488.414 (45)	6330.648 (120)	6480.727 (147)	6448.981 (270)
B' (MHz)	6456.297 (45)	6299.431 (117)	6449.294 (144)	6417.538 (265)
D'' (kHz)	1.962 (6)	1.881 (31)	2.100 (46)	1.802 (220)
D' (kHz)	1.995 (6)	1.914 (33)	2.109 (50)	1.817 (206)
s (cm ⁻¹) ^b	7.01×10^{-4}	9.62×10^{-4}	9.80×10^{-4}	9.65×10^{-4}
	(01 ^{1e} 0)→(01 ^{1e} 1)		(01 ^{1f} 0)→(01 ^{1f} 1)	
	orig. ^c	rev. ^d	orig. ^c	rev. ^d
$\tilde{\nu}_0$ (cm ⁻¹)	2040.203 30 (22)	2040.634 35(30)	2040.202 37(23)	2040.633 78(30)
B'' (MHz)	6522.773 (87)	6491.350 (163)	6531.090 (96)	6499.226 (181)
B' (MHz)	6491.184 (84)	6459.864 (159)	6499.548 (96)	6467.686 (180)
D'' (kHz)	2.052 (16)	2.074 (80)	1.992 (19)	1.806 (89)
D' (kHz)	2.084 (17)	2.046 (77)	2.024 (19)	1.796 (88)
s (cm ⁻¹) ^b	8.40×10^{-4}	8.41×10^{-4}	9.38×10^{-4}	9.07×10^{-4}
	(200)→(201)		(02 ^{2f} 0)→(02 ^{2f} 1)	
	orig. ^c	rev. ^e	orig. ^c	rev. ^e
$\tilde{\nu}_0$ (cm ⁻¹)	2046.640 66 (38)	2047.495 58(46)	2032.898 83(30)	2033.766 66(38)
B'' (MHz)	6470.930 (252)	6407.592 (498)	6564.439 (264)	6502.382 (554)
B' (MHz)	6439.302 (246)	6375.911 (480)	6533.503 (258)	6471.315 (563)
D'' (kHz)	2.330 (118)	2.194 (530)	2.156 (128)	2.014 (630)
D' (kHz)	2.403 (128)	2.137 (488)	2.202 (138)	1.821 (639)
s (cm ⁻¹) ^b	1.10×10^{-3}	1.10×10^{-3}	1.08×10^{-3}	1.07×10^{-3}

^aThe standard errors in parentheses for the revised spectroscopic constants are computed using the estimated 7×7 covariance matrices, multiplied by mean square residuals s^2 , for the sixth-order polynomial fits, taking into account the way each spectroscopic constant depends on more than one polynomial coefficient. (See pp. 83 in Ref. 28.)

^bRoot-mean square residuals for the fitted curves.

^cOriginal analysis of FTIR data (Ref. 2).

^dRevised value obtained by shifting m to $m-1$, still using data of Ref. 2.

^eRevised value obtained by shifting m to $m-2$, still using data of Ref. 2.

already in Ref. 6. We thus expect that a treatment of correlation beyond CCSD(T) would be required to make a substantial improvement in the accuracy of the *ab initio* bond distance predictions.

The CCSD(T)/cc-pVQZ fundamental frequencies obtained by second-order perturbation theory¹⁶ are ν_1 (NS stretching)=740.6 cm⁻¹, ν_2 (NNS bending)=468.1 cm⁻¹, and ν_3 (NN stretching)=2061 cm⁻¹, differing from corresponding variational results by only 0.05, 0.0, and 1.2 cm⁻¹, respectively. The variational result for the NN stretching frequency ($\nu_3=2060.4$ cm⁻¹) at the CCSD(T)/cc-pVQZ level is still too large by 12.4 cm⁻¹, compared to the high resolution result of Brown *et al.*² It is not likely that the difference between theory and experiment in the NN stretching frequency ν_3 would be reduced by extending the basis set, since in the CCSD(T) calculations the ν_3 value tends to increase as the basis set is extended. The NS stretching frequency ν_1 at the CCSD(T)/cc-pVQZ level is smaller than the solid Ar matrix value (752 cm⁻¹)³ by 11 cm⁻¹. Matrix effects, however, in this frequency could easily exceed the ~ 8 cm⁻¹ found in the ν_3 band (Table II). As the basis set is extended from cc-pVTZ to cc-pVQZ, all the vibrational frequencies increase. The NS stretching frequency ν_1 , which increases by 8.7 cm⁻¹, is affected most, while the other frequencies shift by only 3–4 cm⁻¹. No direct measurement of the bend-

ing frequency is available. An estimate of ω_2 based on the l -doubling constant q was suggested in Ref. 2, but the inadequacy of the approximation used there (namely omitting the terms involving the coriolis zeta constants) has already been discussed fully in Ref. 6. In fact the agreement of our calcu-

TABLE IV. Variationally calculated rotational constants (MHz) using the CCSD(T)/cc-pVQZ potential energy function for NNS compared to experiment.

Constants	CCSD(T)	FTIR(orig.) ^a	Δ^b	FTIR(rev.) ^c	Δ^d
B_{000}	6432.7	6488.4	55.7		
B_{001}	6401.5	6456.3	54.8		
B_{010}	6439.2	6526.9	83.3	6495.3	56.1
B_{100}	6392.5	6480.7	88.2	6449.0	56.5
B_{101}	6361.0	6449.3	88.3	6417.5	56.5
B_{011}	6408.4	6495.4	87.0	6463.8	55.4
$B_{02^2f_0}$	6445.4	6564.4	119.0	6502.4	57.0
$B_{02^2f_1}$	6415.6	6533.5	117.9	6471.3	55.7
B_{200}	6351.1	6470.9	119.8	6407.6	56.5
B_{201}	6294.1	6439.3	145.2	6375.9	81.8

^aOriginal analysis of FTIR data (Ref. 2).

^b Δ =FTIR (orig.)-CCSD(T).

^cRevised values obtained by shifting m values (see text).

^d Δ =FTIR(rev.)-CCSD(T).

TABLE V. The CCSD(T) force fields for NNS in internal coordinates (aJ Å⁻ⁿ).

Force constant ^a	CCSD(T)/cc-pVTZ	CCSD(T)/cc-pVQZ	Force constant ^a	CCSD(T)/cc-pVTZ	CCSD(T)/cc-pVQZ
f_{rr}	18.061 6	18.143 7	f_{rrrr}	828.870 2	834.809 1
f_{rR}	1.347 7	1.394 8	f_{rrrR}	-4.380 4	-4.628 2
f_{RR}	5.038 5	5.154 5	f_{rrRR}	7.362 2	8.058 4
$f_{\theta\theta}$	0.551 9	0.555 6	f_{rRRR}	2.922 0	3.565 5
f_{rrr}	-136.295 6	-136.865 8	f_{RRRR}	179.897 0	182.079 8
f_{rrR}	-2.526 3	-2.568 0	$f_{rr\theta\theta}$	-0.459 1	-0.423 1
f_{rRR}	-0.748 6	-0.990 9	$f_{rR\theta\theta}$	2.456 1	2.409 6
f_{RRR}	-36.426 8	-37.044 6	$f_{RR\theta\theta}$	1.637 4	1.616 9
$f_{r\theta\theta}$	-0.943 3	-0.956 2	$f_{\theta\theta\theta\theta}$	1.186 1	1.248 3
$f_{R\theta\theta}$	-1.140 3	-1.141 5			

^aThe force constants are defined such that

$$V(r_1, r_2, r_3) - V_e = (1/2!) \sum_{ij} f_{ij} \Delta r_i \Delta r_j + (1/3!) \sum_{ijk} f_{ijk} \Delta r_i \Delta r_j \Delta r_k + (1/4!) \sum_{ijkl} f_{ijkl} \Delta r_i \Delta r_j \Delta r_k \Delta r_l + \dots$$

lated q (computed with the ζ 's properly accounted for) with the experimental one (Table II), as well as the similar agreement for the other second-order constants, can be taken as the best confirmation that the theoretical value of ω_2 is reasonably accurate. Of the two anharmonicity parameters which can be extracted from the FTIR analysis, it can be seen that the variational method provides a significantly closer theoretical value than the second-order perturbation theory in the case of X_{13} , while for X_{23} both methods are satisfactory, but the perturbation theory result gives somewhat closer agreement.

The CCSD(T)/cc-pVXZ ($X=T$ or Q) force fields up to quartic order are shown in Table V. In fact our CCSD(T)/cc-pVTZ force constants show some deviations from the ones obtained in Ref. 7 with the same method. These deviations are mainly due to the fact that in the force field calculations in Ref. 7 more quintic and sextic terms were included in the expansion of the potential energy surface, resulting in differences of 4.9 and -5.4 cm⁻¹ between their calculated values of ν_2 and ν_3 and our CCSD(T)/cc-pVTZ results.

Ro-vibrational energy levels of NNS up to 4100 cm⁻¹, determined by variational methods using the CCSD(T)/cc-pVQZ PEF, are tabulated in Table VI and compared to the second-order perturbation results. The band origins of the fundamental, first overtone, and simple combination bands calculated by perturbation theory are in excellent agreement with the variational results, with deviations of at most 1.5 cm⁻¹. In fact the only one of the levels involved in the observed FTIR bands that exhibits a significant perturbation by a nearly degenerate level, i.e., that shows a clear difference between the variational and perturbation theory results, is the (201) state, which is close to the (500) level. Inspection of Table III reveals that the origin of the corresponding hot band is indeed shifted by about 6 cm⁻¹ from where it would have been expected by simply extrapolating the positions of the fundamental band and the $\nu_1=1$ hot band, and that the direction of this shift is consistent with the shift of the (201) level in Table VI. The magnitude of the perturbation, however, is overestimated by the variational calculation. Similarly in Table IV the rotational constant B_{201} has a Δ value that is quite different from those for all other vibrational states observed. The FTIR value is very close to the expected

unperturbed value, but the CCSD(T) value of B_{201} is about 25 MHz away from the value that would be extrapolated from less excited vibrational states. Thus the perturbation effect on the rotational constant of this state is also overestimated by the variational calculation.

IV. ELECTRIC DIPOLE MOMENT FUNCTIONS AND FIELD GRADIENTS

Dipole moments calculated by a finite field method at the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ levels of theory were fit to polynomials similar to Eq. (1)

$$\mu_m = \sum_{ijk} D_{ijk}^m (S_1)^i (S_2)^j (S_3)^k, \quad m = z \text{ or } x, \quad (2)$$

where the reference geometries used to expand the EDMFs in Eq. (2) are the equilibrium ones obtained by the CCSD(T) calculations with the corresponding basis set. The CCSD(T)/cc-pVQZ EDMF was used to calculate the dipole moment matrix elements, using rotational-vibrational wave functions obtained from the variational calculations. The band intensity S is given by³²

$$S = \nu \frac{4\pi^2 N_A}{3\hbar c^2} |\langle \nu_1 \nu_2 \nu_3 | \boldsymbol{\mu} | 000 \rangle|^2 \quad (\text{cgs units}), \quad (3)$$

$$S(\text{km/mol}) = 16.1941$$

$$\times \nu(\text{cm}^{-1}) |\langle \nu_1 \nu_2 \nu_3 | \boldsymbol{\mu}(\text{a.u.}) | 000 \rangle|^2.$$

The CCSD(T) EDMFs in the Eckart frame are displayed in Table VII. The CCSD(T) equilibrium dipole moments μ_e are 0.043 D (cc-pVTZ) and 0.081 D (cc-pVQZ). The CCSD(T)/cc-pVQZ dipole moment is 0.056 D in the ground vibrational state, slightly less than μ_e . As pointed out in Ref. 6 the theoretical value of μ_e has tended to decrease sharply as the level of calculation has improved. The sign of the dipole moment, however, is opposite in most of the lower level calculations (sulfur end negative) compared to the two theory levels given in Table VII (sulfur end positive). (Actually only the magnitude of the dipole moment is given in Ref. 6, although the predicted direction is apparently not the same for all levels of theory tabulated there.) Thus μ_e has already passed through zero and further improvements in ba-

TABLE VI. The CCSD(T)/cc-pVQZ vibrational band origins (cm^{-1}) and infrared band intensities S (km/mol) for NNS.

Band			CCSD(T)/cc-pVQZ		Experiment		$S_{\text{calc.}}$
ν_1	$\nu_2^{l_2}$	ν_3	Var.	Pert.	FTIR ^a	IR (matrix) ^b	
0	1 ¹	0	463.10	463.1			0.01
1	0 ⁰	0	740.65	740.7		752	38.59
0	2 ⁰	0	925.57	926.0			4.24
1	1 ¹	0	1198.77	1198.5			5.56E-05
0	3 ¹	0	1388.89	1390.1			7.02E-04
2	0 ⁰	0	1466.37	1466.5			0.05
1	2 ⁰	0	1655.84	1656.2			0.06
0	4 ⁰	0	1851.08	1853.8			0.01
2	1 ¹	0	1919.78	1919.1			2.43E-03
0	0 ⁰	1	2061.40	2061.6	2047.59	2039	385.82
1	3 ¹	0	2113.89	2114.9			7.99E-04
3	0 ⁰	0	2176.96	2177.5			0.38
2	2 ⁰	0	2371.70	2371.5			5.71E-04
0	1 ¹	1	2517.96	2518.0			0.59
3	1 ¹	0	2625.85	2624.8			6.25E-04
1	0 ⁰	1	2804.47	2806.0			2.42
4	0 ⁰	0	2872.71	2873.6			0.03
0	2 ⁰	1	2974.67	2974.2			0.05
3	2 ⁰	0	3072.85	3072.0			1.08E-04
1	1 ¹	1	3255.82	3257.1			2.85E-04
2	0 ⁰	1	3526.52	3535.5			0.07
5	0 ⁰	0	3558.46	3554.9			0.02
1	2 ⁰	1	3706.65	3708.0			7.88E-03
4	2 ⁰	0	3759.80	3757.6			2.75E-04
0	4 ⁰	1	3889.36	3888.5			7.47E-04
0	0 ⁰	2	4095.57	4096.2			3.83

^aReference 2.^bReference 3.TABLE VII. The CCSD(T) EDMFs μ_z and μ_x for NNS (in a.u.).

i	j	k^a	D_{ijk}^z		i	j	k	D_{ijk}^x	
			cc-pVTZ ^b	cc-pVQZ ^c				cc-pVTZ	cc-pVQZ
0	0	0 ^d	0.016 9	0.031 9	0	0	1	0.041 8	0.011 0
1	0	0	1.198 2	1.221 2	1	0	1	-0.442 0	-0.442 6
0	1	0	-0.902 7	-0.923 7	0	1	1	0.021 7	0.035 8
2	0	0	-0.393 4	-0.388 8	2	0	1	-0.003 6	0.010 9
1	1	0	-0.060 8	-0.071 5	1	1	1	0.003 6	-0.019 1
0	2	0	0.084 2	0.094 6	0	2	1	0.062 9	0.072 6
0	0	2	-0.375 1	-0.389 0	0	0	3	-0.012 0	0.015 8
3	0	0	-0.542 4	-0.546 5	3	0	1	0.082 4	0.074 5
2	1	0	1.076 9	1.092 7	2	1	1	-0.016 2	-0.033 0
1	2	0	-0.684 2	-0.682 7	1	2	1	0.251 9	0.203 7
0	3	0	0.128 0	0.134 6	0	3	1	-0.022 5	-0.012 0
1	0	2	0.272 3	0.274 0	1	0	3	0.107 1	0.074 5
0	1	2	0.268 2	0.268 1	0	1	3	-0.030 0	-0.040 1
4	0	0	0.399 2	0.407 6					
3	1	0	-1.042 0	-1.032 6					
2	2	0	1.160 2	1.129 1					
1	3	0	-0.707 4	-0.686 0					
0	4	0	0.155 8	0.143 7					
2	0	2	-0.081 4	-0.092 4					
1	1	2	-0.245 4	-0.213 4					
0	2	2	0.079 9	0.058 7					
0	0	4	-0.111 7	-0.107 0					

^aThe indices i , j , and k are defined in Eq. (1) of the text.^bExpanded about $r(\text{NN})=2.138\ 110a_0$, $R(\text{NS})=3.020\ 803a_0$, $\theta=180.0^\circ$.^cExpanded about $r(\text{NN})=2.132\ 398a_0$, $R(\text{NS})=3.005\ 359a_0$, $\theta=180.0^\circ$.^dThe positive polarity of the equilibrium dipole moments denotes N^-NS^+ , and all EDMFs are expressed in an Eckart frame (see the text).

sis set or correlation treatment may now actually increase the predicted magnitude of μ_e slightly. This suggests that observation of the rotational spectrum of NNS will be difficult but possible. Since low J transitions may be detected first, especially if nozzle expansion sources are studied, we have also predicted the nuclear quadrupole coupling constants at the three atoms at the estimated equilibrium geometry [$r(\text{NN}) = 1.1307 \text{ \AA}$ and $R(\text{NS}) = 1.5782 \text{ \AA}$] using CMRCI with the same cc-pVQZ basis set. This gives the following results for the field gradient parameter q_0 (a.u.) and the coupling constant eq_0Q (MHz): outer $^{14}\text{N}(-0.517/-2.49)$, inner $^{14}\text{N}(-0.312/-1.50)$, and $^{33}\text{S}(3.547/-53.35)$. This would predict complex resolved hyperfine structure for the lowest rotational transitions of the normal isotopic species, with somewhat comparable contributions from both ^{14}N nuclei. For calibration of these predictions we carried out identical calculations on OCS yielding $eq_0Q(^{17}\text{O}) = -1.18 \text{ MHz}$ [experimental value -1.32 MHz (Ref. 33)] and $eq_0Q(^{33}\text{S}) = -25.5 \text{ MHz}$ [experimental value -29.12 MHz (Ref. 33)]. [The coupling constant eq_0Q (MHz) is calculated by multiplying 234.97 times the electric field gradient ($q_0 = -q_{zz}$, a.u.) times the nuclear electric quadrupole moment (barns). All values of Q were obtained from Ref. 34, except for $Q(^{14}\text{N})$, which was taken from Ref. 35.]

The absolute intensities corresponding to various vibrational band origins at the CCSD(T)/cc-pVQZ level of theory are shown in Table VI. The already observed ν_3 band is stronger than the ν_1 band by a factor of 10, and the ν_1 band is in turn stronger than the $2\nu_3$ and $2\nu_2$ bands by about same factor. The intensity of the bending fundamental is predicted to be practically zero. Thus it appears that infrared spectroscopic observation of the NS stretching fundamental should definitely be feasible, but for the bending mode, observation of the first overtone band seems to be the only realistic opportunity for infrared spectroscopy.

ACKNOWLEDGMENTS

This work was supported by the Experimental Physical Chemistry Program of the National Science Foundation. K.A.P. acknowledges the support of the National Science Foundation (CHE-9501262) and the Division of Chemical Sciences in the Office of Basic Energy Sciences of the U.S. Department of Energy at Pacific Northwest Laboratory, a multiprogram national laboratory operated by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830. The authors would like to thank D. McNaughton for a careful reading of this paper and for his helpful comments.

- ¹C. Wentrup, S. Fischer, A. Maquestiau, and R. Flammang, *J. Org. Chem.* **51**, 1908 (1986).
- ²R. D. Brown, P. S. Elmes, and D. McNaughton, *J. Mol. Spectrosc.* **140**, 390 (1990).
- ³P. Kambouris, T.-K. Ha, and C. Wentrup, *J. Phys. Chem.* **96**, 2065 (1992).
- ⁴P. Hassanzadeh and L. Andrews, *J. Am. Chem. Soc.* **114**, 83 (1992).
- ⁵R. D. Davy and H. F. Schaefer III, *J. Am. Chem. Soc.* **113**, 1917 (1991).
- ⁶C. L. Collins, Y. Yamaguchi, and H. F. Schaefer III, *J. Chem. Phys.* **98**, 4777 (1993).
- ⁷A. T. Wong and G. B. Bacskay, *Chem. Phys. Lett.* **217**, 17 (1994).
- ⁸K. Ragavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- ⁹J. Tennyson, S. Miller, and C. R. Le Sueur, *Comput. Phys. Commun.* **75**, 339 (1993); J. R. Henderson and J. Tennyson, *ibid.*, 365.
- ¹⁰C. R. Le Sueur, S. Miller, J. Tennyson, and B. T. Sutcliffe, *Mol. Phys.* **76**, 1147 (1992).
- ¹¹T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ¹²D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- ¹³C. Hampel, K. A. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).
- ¹⁴M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).
- ¹⁵MOLPRO is a suite of *ab initio* programs written by H.-J. Werner and P. J. Knowles with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, E. A. Reinsch, A. J. Stone, and P. R. Taylor.
- ¹⁶I. M. Mills, *Molecular Spectroscopy: Modern Research*, edited by K. N. Rao and C. W. Mathews (Academic, New York, 1972).
- ¹⁷J. Senekowitsch, Ph.D. Thesis, Universität Frankfurt, Germany, 1988.
- ¹⁸C. Eckart, *Phys. Rev.* **47**, 552 (1935).
- ¹⁹W. C. Ermler and B. J. Krohn, *J. Chem. Phys.* **67**, 1360 (1979).
- ²⁰S. M. Adler-Golden and G. D. Carney, *Chem. Phys. Lett.* **113**, 582 (1985).
- ²¹H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- ²²P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).
- ²³H. J. Werner, *Adv. Chem. Phys.* **59**, 1 (1987).
- ²⁴H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
- ²⁵P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ²⁶J.-G. Lahaye, R. Vandenhoute, and A. Fayt, *J. Mol. Spectrosc.* **123**, 48 (1987).
- ²⁷M. Polak, M. Gruebele, and R. J. Saykally, *J. Chem. Phys.* **87**, 3352 (1987).
- ²⁸N. Draper and H. Smith, *Applied Regression Analysis*, 2nd Ed. (Wiley-Interscience, New York, 1981).
- ²⁹K. A. Peterson and T. H. Dunning, Jr., *J. Phys. Chem.* **99**, 3898 (1995).
- ³⁰K. A. Peterson, unpublished results.
- ³¹K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic molecules* (Van Nostrand, Princeton, 1979).
- ³²M. A. H. Smith, C. P. Rinsland, B. Fridovich, and K. N. Rao, *Molecular Spectroscopy: Modern Research*, edited by K. N. Rao (Academic, New York, 1985), Vol III.
- ³³A. Maki and D. R. Johnson, *J. Mol. Spectrosc.* **47**, 226 (1973).
- ³⁴*Tables of Isotopes*, edited by C. M. Lederer and V. S. Shirley (Wiley, New York, 1978), 7th ed.
- ³⁵P. L. Cumming, G. B. Bacskay, N. S. Hush, and R. Ahlrichs, *J. Chem. Phys.* **86**, 6908 (1987).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/jcpo/jcpcr/jsp>
Copyright of Journal of Chemical Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/jcpo/jcpcr/jsp>