

The bending frequency δ_{NS} of dinitrogen sulfide (N_2S): A theoretical analysis demonstrating the importance of Coriolis coupling terms

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There exists a discrepancy between theory and experiment for the N_2S bending vibrational frequency. *Ab initio* molecular electronic structure theory has been used in order to investigate the electronic ground state of the dinitrogen sulfide (N_2S) molecule. Self-consistent field (SCF), configuration interaction with single and double excitations (CISD), coupled cluster with single and double excitations (CCSD) wave functions were employed using the three basis sets, the double zeta plus polarization (DZP), triple zeta plus double polarization (TZ2P), and TZ2P with one set of higher angular momentum polarization functions (TZ2Pf). For CCSD wave functions the connected triple excitations were included through perturbation theory [CCSD(T)]. Using the CCSD(T) method with the larger basis sets, experimental physical properties including bond lengths, rotational constant, centrifugal distortion constant, *l*-type doubling constant, vibrational frequencies, and isotopic shifts for the N–N stretching frequency have been reproduced with quantitative accuracy. This analysis proves the essential correctness of an earlier theoretical prediction of the N_2S harmonic bending vibrational frequency.

I. INTRODUCTION

In 1975 Powell postulated the existence of N_2S as the carrier of the spectroscopic features in a $\text{N}_2\text{--CS}_2$ laser system.¹ By careful comparison of known structures and vibrational frequencies for molecules similar to the suggested "linear" N_2S , Powell estimated the rotational constant (B_0) and N–N stretching frequency to be ~ 0.21 and 2000 cm^{-1} , respectively. The N_2S species was first definitively observed in 1986 by Wentrup, Fischer, Maquestiau, and Flammang² as the product of the flash vacuum pyrolysis (FVP) of 5-phenyl-1,2,3,4-thiaziazole. This compound was detected by infrared (IR) spectroscopy and mass spectrometry. The N–N stretching vibration was located at 2030 cm^{-1} , which is close to the value predicted by Powell.¹ In 1988 Bender, Carnovale, Peel, and Wentrup³ studied the N_2S by photoelectron spectroscopy and determined the ionization energies (IEs) for the three highest lying occupied molecular orbitals.

In 1990 Brown, Elmes, and McNaughton employed the FVP method to obtain the high-resolution gas-phase IR spectrum of the N_2S molecule.⁴ They were able to precisely identify the N–N stretching mode at 2047.59 cm^{-1} and to determine the bond lengths $r_0(\text{NN}) = 1.1388\text{ \AA}$ and $r_0(\text{NS}) = 1.5775\text{ \AA}$. Their effective rotational constant B'' (3_0^1 vibrational band) was 0.2164 cm^{-1} and the equilibrium B value (B_e) was 0.2158 cm^{-1} , both being again close to Powell's predicted value¹ of 0.21 cm^{-1} . In a recent paper Hassanzadeh and Andrews⁵ reported detection of the N–N stretching vibration for N_2S at 2040 cm^{-1} using the matrix isolation IR technique and they also showed vibrational frequencies for isotopomers. Very recently Kambouris, Ha, and Wentrup⁶ reinvestigated the matrix-isolation IR spectrum of N_2S and located two vibrations at 2039 cm^{-1} for the N–N stretch and at 752 cm^{-1} for the N–S stretch.

There have been several *ab initio* theoretical studies on the N_2S molecule.^{3,4,6–9} Most of the studies were at the Roothaan–Hall^{10,11} self-consistent field (SCF) level of theory or Møller–Plesset perturbation theory¹² to second (MP2) or third order (MP3). In our previous paper⁹ configuration interaction with single and double excitations (CISD) and coupled cluster with single and double excitations (CCSD) methods as well as the SCF wave function were employed. All these theoretical studies unequivocally have shown the linear NNS to be the lowest energy isomer. However, Kambouris, Ha, and Wentrup⁶ noted emphatically in their recent paper that there was still a non-negligible discrepancy between experiment and theory regarding both structure and vibrational frequencies. The present study attempts to narrow the discrepancy between experiment and theory using higher levels of theory than those employed in previous theoretical work.

II. THEORETICAL CONSIDERATIONS

In this section the electron configuration of the linear N_2S molecule is first described and the equations required to evaluate various rotation–vibrational properties are then briefly reviewed.

A. Electron configuration

The N_2S molecule contains sixteen (16) valence electrons and it is isovalent to the more familiar CO_2 , N_2O , and COS molecules. According to Walsh's rules¹³ N_2S is expected to be linear, and it has been proven to be linear in its electronic ground state. The electronic configuration of the ground state $^1\Sigma^+$ of N_2S is^{3,4,6–9}

$$[\text{core}](6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^4, \quad (1)$$

where [core] abbreviates the lower-lying seven core orbitals. Among the six occupied valence orbitals the 6σ orbital

describes mainly the N–N σ bond and the 7σ orbital the N–S σ bond. The 2π orbital represents two N–N π bonds, whereas the 3π orbital yields two nonbonding orbitals mainly localized on the S atom. The 8σ and 9σ orbitals are related to the nonbonding orbitals along the molecular axis, the former being localized mainly on the S atom and the latter on the N atom. Thus the electron configuration of N_2S may be schematically written as



or



The MO ordering in Eq. (1) is deduced from the orbital energies at the SCF level of theory, and appears to be consistent with the IEs determined via photoelectron spectroscopy by Bender, Carnovale, Peel, and Wentrup.³ According to the analysis by these authors,³ the N–S bond is relatively weak so that the S atom affects only a small perturbation of the σ_g and π_u MOs of N_2 within the linear N_2S molecule.

B. Rotational constant

The equilibrium rotational constant B_e is given by

$$B_e = \hbar^2 / 2hcI_e, \quad (4)$$

where $I_e (= I_{xx} = I_{yy})$ is the equilibrium moment of inertia (the molecule is assumed to lie along the z axis).

C. Coriolis zeta constant

The Coriolis zeta constants, ξ_{rs} , which couple the normal coordinates Q_r to Q_s through rotation about the α axis, are defined by

$$\xi_{rs}^\alpha = \sum_i (L_{ir}^\beta L_{is}^\gamma - L_{ir}^\gamma L_{is}^\beta), \quad (5)$$

where α , β , and γ are cyclic permutations of x , y , and z , and L is the matrix which transforms the normal coordinates to mass-weighted Cartesian coordinates.

D. Quartic centrifugal distortion constant

The quartic centrifugal distortion constant, D_J , is expressed as

$$D_J = \frac{1}{2} \sum_s \frac{B_s^2}{\omega_s}, \quad (6)$$

where the summation is restricted to totally symmetric normal modes. The rotational derivatives B_s , appearing in Eq. (6) are defined as¹⁴⁻¹⁶

$$B_s = B_s^{xx} = B_s^{yy} = -\frac{\hbar^3}{2h^{3/2}c^{3/2}\omega_s^{1/2}I_e^2} a_s, \quad (7)$$

where the inertial derivatives over the normal coordinates, a_s , are defined by

$$a_s = \left(\frac{\partial I_{xx}}{\partial Q_s} \right)_e = \left(\frac{\partial I_{yy}}{\partial Q_s} \right)_e. \quad (8)$$

Note that the inertial derivatives in Eq. (8) are nonzero only for totally symmetric modes.

E. Rotational l -type doubling constant

The rotational l -type doubling constant q_l associated with a degenerate vibration ω_l of a linear molecule has been observed to be v , J , and k dependent,¹⁷⁻²⁰ but in the present study only the equilibrium term, q_l^e , is considered. The q_l^e values are given by

$$q_l^e = -\frac{2B_e^2}{\omega_l} \sum_s \xi_{st}^2 \frac{3\omega_l^2 + \omega_s^2}{\omega_l^2 - \omega_s^2}, \quad (9)$$

where the summation is restricted to nondegenerate normal modes. Using the relationship for the linear N_2S molecule

$$(\xi_{21}^x)^2 + (\xi_{23}^x)^2 = 1, \quad (10)$$

Eq. (9) may be rewritten as

$$q_2^e = \frac{2B_e^2}{\omega_2} \left[1 + (\xi_{21}^x)^2 \frac{4\omega_2^2}{\omega_1^2 - \omega_2^2} + (\xi_{23}^x)^2 \frac{4\omega_2^2}{\omega_3^2 - \omega_2^2} \right], \quad (11)$$

where the zeta constants are defined in Eq. (5). By convention the N–S harmonic stretching frequency is designated as ω_1 , NNS bending frequency as ω_2 , and N–N stretching frequency as ω_3 .

III. THEORETICAL PROCEDURES

In this study four basis sets have been employed. The double zeta (DZ) part of the basis set is Dunning's double-zeta contraction^{21,22} of Huzinaga's primitive sets^{23,24} and is designated as N ($9s5p/4s2p$) and S ($11s7p/6s4p$). The addition of one set of Cartesian d functions to the N and S DZ basis set with orbital exponents $\alpha_d(N) = 0.80$ and $\alpha_d(S) = 0.50$ forms the DZP basis set. The triple zeta (TZ) part of the basis set is Dunning^{21,22} and McLean and Chandler's²⁵ triple-zeta contraction of Huzinaga's primitive sets^{23,24} and is designated as N ($10s6p/5s3p$) and S ($12s9p/6s5p$). The addition of two sets of Cartesian d functions to the N and S basis set with orbital exponents $\alpha_d(N) = 1.60$, 0.40 and $\alpha_d(S) = 1.40$, 0.350 creates the TZ2P basis set. The third and fourth basis sets are the TZ2P basis set supplemented with one set of higher angular momentum polarization functions $\alpha_f(N) = 1.0$ and $\alpha_f(S) = 0.55$, denoted TZ2Pf, and two sets of higher angular momentum polarization functions $\alpha_f(N) = 2.0$, 0.25 and $\alpha_f(S) = 1.10$, 0.275 , termed TZ2P2f. Complete sets of six Cartesian d -like functions and ten f -like functions were used throughout. The largest basis set, consisting of 145 contracted Gaussian functions, TZ2P2f, was used only with the SCF method.

Electron correlation effects were included by employing both the configuration interaction (CI) and coupled cluster (CC) methods. Only the valence electrons were explicitly correlated; thus the seven lowest occupied molecular orbitals (N, $1s$ -like; S, $1s$, $2s$; and $2p$ -like) were held doubly occupied (frozen cores) and the three highest lying virtual orbitals (N, $1s^*$ -like; S, $1s^*$ -like) were excluded (deleted virtuals) from the CI and CC procedures. Other-

TABLE I. Theoretical predictions of the molecular structure and physical properties for the linear NNS ($^1\Sigma^+$).^a

Level of theory	Energy	r_e (N–N)	r_e (N–S)	μ_e	B_e	D_e $\times 10^7$	q_2^c $\times 10^3$	ω_1 σ^+	ω_2 π	ω_3 σ^+
SCF/DZP	–506.387 45	1.0882	1.6599	1.160	0.2086	0.9489	0.3528	588(41.1)	481(3.1)	2571(291.3)
SCF/TZ2P	–506.443 95	1.0732	1.6528	1.216	0.2117	1.0000	0.3860	586(41.4)	495(1.7)	2587(284.9)
SCF/TZ2Pf	–506.452 06	1.0755	1.6375	1.166	0.2141	0.9597	0.3604	608(47.4)	497(1.5)	2571(309.4)
SCF/TZ2P2f	–506.453 11	1.0747	1.6376	1.182	0.2142	0.9535	0.3623	611(49.1)	501(1.6)	2574(314.6)
CISD/DZP	–506.794 31	1.1234	1.6200	0.391	0.2110	0.6751	0.2744	714(54.5)	478(1.5)	2286(390.3)
CISD/TZ2P	–506.890 25	1.1013	1.6148	0.474	0.2148	0.7384	0.2888	700(56.8)	488(0.7)	2327(401.9)
CISD/TZ2Pf	–506.943 17	1.1032	1.5973	0.393	0.2176	0.7106	0.2863	728(59.9)	497(0.6)	2327(418.7)
CCSD/DZP	–506.849 08	1.1385	1.6219	0.203	0.2088	0.6592	0.2712	713(48.1)	459(0.9)	2162(358.0)
CCSD/TZ2P	–506.952 03	1.1148	1.6180	0.296	0.2124	0.7273	0.2852	695(50.5)	469(0.4)	2203(376.4)
CCSD/TZ2Pf	–507.012 46	1.1173	1.6002	0.214	0.2152	0.7010	0.2836	723(52.7)	477(0.3)	2204(386.7)
CCSD(T)/DZP	–506.872 40	1.1518	1.6125	0.204	0.2087	0.6038	0.2649	748(35.9)	451(0.2)	2052(391.4)
CCSD(T)/TZ2P	–506.982 16	1.1291	1.6079	0.109	0.2123	0.6646	0.2772	730(40.5)	459(0.04)	2075(418.3)
CCSD(T)/TZ2Pf	–507.047 04	1.1320	1.5910	0.177	0.2149	0.6442	0.2762	757(39.8)	469(0.03)	2080(413.4)
Expt. ^b		1.1388	1.5775		0.2158	0.6543	0.2714		$\approx 343(-)$	2048(-)
Expt. ^c										2040(-)
Expt. ^d								752(<i>w</i>)		2039(<i>s</i>)

^aEnergy in hartree, bond lengths in Å, dipole moment in debye, rotational constant, centrifugal distortion constant, *l*-type doubling constant and harmonic vibrational frequencies in cm^{-1} , and infrared intensities (in parentheses) in km mol^{-1} .

^bThe structural parameters and fundamental vibrational frequencies are from Ref. 4. The bond lengths are the r_0 values.

^cThe fundamental vibrational frequency is from Ref. 5.

^dThe fundamental vibrational frequency is from Ref. 6.

wise, all single and double excitations from the SCF reference configuration were included (CISD and CCSD). With the TZ2Pf basis set the CISD and CCSD wave functions for the $^1\Sigma^+$ state N_2S in C_{2v} and C_s symmetry involved 80 277 and 155 743 configurations, respectively.

The CISD wave functions were determined via the shape driven graphical unitary group approach.²⁶ The CC method employed was the closed shell single and double excitation (CCSD) approach of Purvis and Bartlett,²⁷ as modified by Scuseria and Janssen.²⁸ Perturbative triple excitations were included using the higher level CCSD(T) method originally proposed by Raghavachari, Trucks, Pople, and Head-Gordon.²⁹ The CCSD(T) methods actually used were those of Scuseria and Lee.³⁰ The C_0 values, the reference configuration coefficients in CI wave functions, with the DZP, TZ2P, and TZ2Pf basis sets were 0.934, 0.932, and 0.931, respectively. On the other hand T_1 values, the Euclidian norms of t_1 amplitudes in the CCSD wave functions,^{31,32} with the three basis sets were 0.0214, 0.0216, and 0.0212, respectively. Although our t_1 diagnostic (T_1 's) are slightly larger than the recommended threshold of 0.020 for a single-reference wave function,^{31,32} all correlated levels of theory (with single-reference) have reproduced the experimental values quite well as shown in the next section.

Analytic gradient techniques³³ were used to determine the equilibrium structures of the N_2S molecule. The second derivatives of the total energy (Hessian) were evaluated analytically for the SCF wave functions^{34–36} and via the finite differences of the analytical gradients for the CISD,^{37,38} CCSD,³⁹ and CCSD(T)⁴⁰ methods. The harmonic vibrational frequencies were obtained by diagonalizing the mass-weighted Hessian matrix. Various rotation–vibrational constants were evaluated using the equations described in the preceding section.

IV. RESULTS AND DISCUSSION

In Table I theoretical predictions of the optimized structure and physical properties as well as available experimental results for the N_2S molecule are presented.

A. Geometry

It should be noted that the experimental bond lengths are the r_0 [average bond length at the $v=(0,0,0)$ level] values⁴ and this r_0 quantity may be somewhat different from the r_e (bond length at the bottom of the potential energy curve) structure. For example for the isovalent N_2O molecule the r_0 (NN) and r_e (NN) values are 1.1286 and 1.1273 Å, while r_0 (NO) and r_e (NO) values are 1.1876 and 1.1851 Å, respectively.^{4,41–46} Thus for the N_2O molecule the differences between r_0 and r_e structures are 0.0013 (1.1286–1.1273) Å for the N–N bond and 0.0025 (1.1876–1.1851) Å for the N–O bond, respectively. Although there are no experimental r_e values, the differences between the r_0 and r_e structures for the N_2S molecule are expected to be <0.003 Å.

At the SCF level of theory the N–N length is underestimated and the N–S bond length is overestimated. Inclusion of the correlation effects significantly increases the N–N bond length and decreases the N–S bond length. This phenomenon may be explained as follows. The most important excitations involved in the configuration interaction space are of double excitation type

$$\cdots(2\pi)^4(3\pi)^4 \rightarrow \cdots(2\pi)^2(3\pi)^4(4\pi)^2. \quad (12)$$

Note that there are three linearly independent $^1\Sigma^+$ configuration state functions of the above orbital occupancy. In Eq. (12) the 2π describes the N–N bonding π orbital, while the 4π designates the N–N antibonding π orbital. Thus the N–N bond length increases upon double electron

excitations in Eq. (12). This increase of N–N bond length elevates the energies of 6σ and 2π orbitals and lowers the energy of the 7σ orbital. Consequently a decrease in the N–S bond length is also accompanied with electronic excitations in Eq. (12).

At the SCF level the N–N bond of N_2S has a strong triple bond character as the N_2 molecule remains relatively intact and the N–S bond has rather weak single bond character. With the TZ2Pf basis set the SCF wave function underestimates the N–N bond length by 0.063 Å and overestimates the N–S bond length by 0.060 Å compared to the experimental r_0 values. On the other hand at the correlated levels the N–N bond is elongated to show a two and a half bond nature and the N–S bond is shortened to display one and a half bond character. Again with the TZ2Pf basis set the CISD, CCSD, and CCSD(T) methods underestimate the N–N bond length by 0.036, 0.022, and 0.007 Å, respectively, whereas they overestimate the N–S bond length by 0.020, 0.023, and 0.014 Å, respectively, relative to experiment. In order to obtain quantitative agreement with the experimental value in the bond lengths, it seems necessary to include higher excitations (more than singles and doubles) and to employ the basis set with the multiple polarization and higher angular momentum polarization functions.

B. Dipole moment

It is remarkable that the predicted dipole moment is 1.17 D at the SCF level, 0.39 D at the CISD level, 0.21 D at the CCSD level, and 0.18 D at the CCSD(T) level of theory with the TZ2Pf basis set. This is one of the strongest known dependencies of dipole moment on correlation effects. With the $C_{\infty v}$ molecular framework the nonvanishing component of the dipole moment should be along the molecular axis. It is seen that electronic excitations perpendicular to the molecular axis in the configuration interaction space, e.g., represented by Eq. (12), decrease the charge separation between the positive and negative poles, substantially reducing the absolute value of the total dipole moment.

C. Rotational constant

The experimental rotational constant presented in Table I is the value at equilibrium⁴; therefore, it may legitimately be directly compared with the theoretical value. The B_e values at the SCF and correlated levels of theory agree quite well with the experimental value, although the length and nature of the N–N and N–S bonds is rather different in the four levels of theory as mentioned in Sec. IV A. For this molecule the B_e value seems to be less sensitive to the level of theory and the basis set.

D. Quartic centrifugal distortion constant

The experimental value for quartic centrifugal distortion constant, D'' , is obtained from the IR spectrum of the ν_3 band (3_0^1 transition) of N_2S .⁴ Although this effective value is not directly comparable with the theoretically determined D_e value, it is obvious that the SCF D_e values are

overestimated relative to the experimental D'' value. On the other hand the CISD and CCSD values are in satisfactory, and the CCSD(T) values are in good agreement with the experiment. It appears to be important to use a reliable geometry and vibrational frequencies to reproduce the experimental centrifugal distortion constant. The D_e quantity is more sensitive to the level of theory than the B_e constant discussed in the preceding section.

E. Rotational l -type doubling constant

The rotational l -type doubling constant has been experimentally determined⁴ to be $0.2714 \times 10^{-3} \text{ cm}^{-1}$. The corresponding theoretical value is obtained using Eq. (11). The SCF q_2^e values are again significantly overestimated compared to the experimental value. On the contrary the CISD and CCSD values show encouraging agreement and the CCSD(T) values display very good agreement with the experimental value. Brown, Elmes, and McNaughton have used this q_2^e value to estimate the ω_2 frequency ignoring Coriolis coupling terms, the second and third terms in the brackets in Eq. (11).⁴ That is, they estimated the ω_2 frequency as

$$\omega_2 \approx \frac{2B_e^2}{q_2^e} \approx \frac{2(0.215\ 809)^2}{0.000\ 271\ 4} \approx 343 \text{ (cm}^{-1}\text{)}. \quad (13)$$

However, it must be pointed out here that the Coriolis coupling terms are *not* small relative to unity as demonstrated in Table II. In fact, at the most reliable TZ2Pf-CCSD(T) level of theory the contribution of the Coriolis coupling terms is 0.402. Including this contribution the ω_2 frequency becomes 481 (343×1.402) cm^{-1} . This "adjusted" experimental harmonic vibrational frequency will be compared with the theoretical value in the next section. The SCF level of theory underestimates the prefactor ($2B_e^2/q_2^e$) and overestimates the Coriolis factor [the sum of the three terms in the brackets in Eq. (11)]. Correlated levels of theory reproduce the experimental prefactor very satisfactorily. However, the CISD and CCSD wave functions somewhat overestimate the Coriolis factor relative to the most reliable CCSD(T) results.

F. Harmonic vibrational frequencies

The experimental N–N stretching frequencies in Table I are fundamental (anharmonic) values and they were observed via the matrix isolation technique^{2,5,6} and gas-phase IR spectroscopy.⁴ The harmonic vibrational frequency for the N–N stretch (ω_3) at the SCF level of theory is substantially overestimated, 25.5%, relative to the experimental fundamental value (gas phase). This large deviation may be attributed to the significant underestimation of the N–N bond length at the SCF level. The bond lengths predicted by the CISD and CCSD wave functions are much closer to the experimental values; longer N–N and shorter N–S bond lengths relative to the SCF values. Accordingly the ω_3 vibrational frequency from the CISD and CCSD methods is significantly improved; however, the deviations are still large, 13.6%, and 7.6%, respectively with the TZ2Pf basis set. At the CCSD(T) level of theory the dis-

TABLE II. Theoretical predictions of the bending frequency (in cm^{-1}) for the N_2S molecule using Eq. (11).^a

Parameter	Coriolis constants		Prefactor	Coriolis factor	Frequency
	ξ_{12}	ξ_{23}			
Level of theory			$(2B_e^2/q_e^2)$		ω_2
SCF/DZP	0.319	0.948	247	1.949	481
SCF/TZ2P	0.317	0.949	232	2.130	495
SCF/TZ2Pf	0.319	0.948	254	1.952	497
SCF/TZ2P2f	0.318	0.948	253	1.979	501
CISD/DZP	0.307	0.952	325	1.474	478
CISD/TZ2P	0.309	0.951	319	1.527	488
CISD/TZ2Pf	0.307	0.952	331	1.501	497
CCSD/DZP	0.300	0.954	321	1.429	459
CCSD/TZ2P	0.304	0.953	316	1.481	469
CCSD/TZ2Pf	0.302	0.953	327	1.461	477
CCSD(T)/DZP	0.285	0.959	329	1.373	451
CCSD(T)/TZ2P	0.292	0.956	325	1.411	459
CCSD(T)/TZ2Pf	0.287	0.958	334	1.402	469
expt. ^b	343	1.000	343

^aCoriolis factor is the sum of the three terms in the brackets in Eq. (11).

^bEstimated fundamental bending frequency is from Ref. 4.

crepancy between theory and experiment is drastically narrowed. The deviation is only 27 cm^{-1} (1.3%) with the TZ2P basis set and 32 cm^{-1} (1.6%) with the TZ2Pf basis set. For the isovalent N_2O molecule the experimental harmonic and fundamental frequencies for the N–N stretch are 2282 and 2224 cm^{-1} , respectively.^{41–45} Thus the anharmonic correction for this mode is -58 ($2224-2282$) cm^{-1} or -2.6% for N_2O relative to the fundamental frequency. For the N_2S molecule the anharmonic correction is considered to be smaller than that for the N_2O molecule. The CCSD(T) harmonic vibrational frequencies 2075 cm^{-1} (TZ2P) and 2080 cm^{-1} (TZ2Pf) should be very close to the “real” (yet undetermined) harmonic frequency.

The N–S stretching frequency was quite recently observed at 752 cm^{-1} in the Ar matrix.⁶ Contrary to the N–N stretching mode, the theoretical frequency for the N–S stretching mode is underestimated by all levels of theory except the TZ2Pf-CCSD(T) method. This underestimation in the frequency is apparently due to overestimation of the N–S bond length by *ab initio* methods used in the present research. The CCSD(T) harmonic vibrational frequencies of 730 cm^{-1} (TZ2P) and 757 cm^{-1} (TZ2Pf) are in very good agreement with the experimental fundamental value of 752 cm^{-1} .

As mentioned in Sec. IV E the experimentally estimated⁴ bending frequency of 343 cm^{-1} is too small. Our “adjusted” experimental bending frequency of 481 cm^{-1} appears to be quite reasonable. At all levels of theory the predicted bending frequency agrees reasonably well with the “adjusted” value of 481 cm^{-1} . However, the apparent good agreement of the SCF frequency may be fortuitous, since the SCF prefactor and Coriolis factor are significantly different from those of the correlated levels of theory (see Table II).

G. Vibrational isotopic shift

In 1992 Hassanzadeh and Andrews were able to observe the N–N stretching frequencies for several iso-

topomers.⁵ The isotope shifts between $^{14}\text{N}^{14}\text{N}^{32}\text{S}$ and $^{14}\text{N}^{15}\text{N}^{32}\text{S}$, $^{15}\text{N}^{14}\text{N}^{32}\text{S}$, and $^{15}\text{N}^{15}\text{N}^{32}\text{S}$ are 36.3 ($2040.2-2003.9$) cm^{-1} , 30.9 ($2040.2-2009.3$) cm^{-1} , and 67.9 ($2040.2-1972.3$) cm^{-1} , respectively. Theoretical estimates for these isotope shifts as well as experimental values are tabulated in Table III. The SCF method was not able to distinguish between the shift to the 14–15–32 and the shift to 15–14–32 isotopomers. However the shift to the 15–15–32 isotopomer was reasonably well reproduced by the SCF wave function. The correlated levels of theory reproduce the isotope shifts very satisfactorily. In particular, the agreement between the experimental and the CCSD(T) values for the isotopic shifts is excellent.

V. CONCLUDING REMARKS

A theoretical investigation on the linear dinitrogen sulfide (N_2S) has been carried out using higher levels of the-

TABLE III. Theoretical predictions of the vibrational isotopic shift (in cm^{-1}) for the N–N stretching mode.

Isotopomer	$^{14}\text{N}^{14}\text{N}^{32}\text{S}$	$^{14}\text{N}^{15}\text{N}^{32}\text{S}$	$^{15}\text{N}^{14}\text{N}^{32}\text{S}$	$^{15}\text{N}^{15}\text{N}^{32}\text{S}$
Level of theory				
SCF/DZP	0.0	43.2	42.9	86.9
SCF/TZ2P	0.0	43.4	43.2	87.4
SCF/TZ2Pf	0.0	43.2	42.9	86.9
SCF/TZ2P2f	0.0	43.2	42.9	87.0
CISD/DZP	0.0	39.7	36.7	77.3
CISD/TZ2P	0.0	40.1	37.7	78.6
CISD/TZ2Pf	0.0	40.4	37.4	78.7
CCSD/DZP	0.0	38.1	34.2	73.0
CCSD/TZ2P	0.0	38.4	35.3	74.5
CCSD/TZ2Pf	0.0	38.7	35.0	74.5
CCSD(T)/DZP	0.0	37.1	31.4	69.3
CCSD(T)/TZ2P	0.0	37.0	32.3	70.1
CCSD(T)/TZ2Pf	0.0	37.5	32.0	70.2
expt. ^a	0.0	36.3	30.9	67.9

^aFundamental vibrational frequencies are from Ref. 5. See text for details (Sec. IV G).

ory and larger basis sets compared to previous work. Equally important, a far more sophisticated analysis of the rotation-vibration problem has been completed. The predicted molecular structure and spectroscopic parameters are found to be considerably sensitive to the level of theory, probably due to existence of closely spaced high-lying occupied and low-lying unoccupied molecular orbitals. As is usually the case for the molecules with multiple bonds, inclusion of higher excitations (higher than singles and doubles), and the use of a basis set augmented with multiple polarization and higher angular momentum polarization functions appears to be essential to accurately describe the multiple bonds of N₂S species. All experimental physical properties studied in the present research have been reproduced with quantitative accuracy employing the CCSD(T) level of theory with the TZ2P and TZ2Pf basis sets.

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