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Ab initio prediction of the vibrational frequencies of N_2S

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Ab initio potential energy surfaces of N_2S, calculated using the CCSD and CCSD(T) methods with the cc-pVTZ basis set, are reported. Both harmonic and anharmonic frequencies of N_2S are predicted in an effort to resolve the large discrepancies between theory and experiment that had been previously noted. The CCSD(T) anharmonic stretch frequencies agree well with experiment, but for the bend a discrepancy of ≈ 100 cm^{-1} remains. Overtone and combination band origins, up to ≈ 4100 cm^{-1}, are also given.

1. Introduction

The existence of dinitrogen sulfide (N_2S) has been experimentally confirmed [1] although, to date, there is only a small amount of spectroscopic data for it. The geometry has been deduced from the rotational band structure [2]. In the gas phase, only the NN stretch band origin has been determined [2], whilst in Ar matrix isolation studies both the NN and NS stretch frequencies have been observed [3,4]. The linear angle bend frequency has been inferred [2] from the rotational band structure. Thus, very little experimental information is available on its potential energy surface and, as yet, there is no experimental estimate of the harmonic frequencies.

N_2S is quite unstable, consequently it is difficult to study by high-resolution gas-phase spectroscopy. Hence ab initio studies may be of considerable value in verifying and predicting aspects of its spectroscopy. Earlier ab initio studies [4–8] were restricted to the study of the harmonic frequencies and the discrepancies between theory and experiment were quite large, especially for the NN stretch. The resolution of these discrepancies has been the primary motivation for our work as we felt that a calculation of both harmonic and anharmonic frequencies using a good quality basis set in conjunction with a high-level treatment of electron correlation would reconcile theory and experiment. As our work was nearing completion, a study by Collins et al. [9] was published that also addresses these problems. Although the work of Collins et al. was restricted to the calculation of harmonic frequencies it resolved much of the above discrepancies and resulted in an accurate equilibrium geometry and a greatly improved NN stretch frequency. Their method is the one used in this work, viz. the coupled-cluster singles and doubles method including the perturbative treatment of triples (CCSD(T)). The effect of the triple excitations has been shown to be very important [9], resulting in significant improvement in the calculated frequencies, as found already in other molecules, including the isovalent nitrous oxide [10,11] and ozone [12]. The available evidence strongly suggests that CCSD(T) has the capacity to accurately describe the energetics of "difficult" molecules for which simpler methods such as MP2 and SDCI may be inadequate.

In this work we report a study of the potential energy surface on N_2S, using the CCSD and CCSD(T) methods. As in our previous work on HCN and N_2O [10,13] we fit the potential energy surface to a sextic Morse coordinate expansion and variationally compute the vibrational states. Thus, we obtain anharmonic band origins, enabling a proper comparison to be made between theory and experiment.

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2. Computational details

The correlation-consistent polarized valence triple zeta (cc-pVTZ) [14,15] basis set has been used for both the N and S atoms: a(10s5p2d1f) primitive set contracted to [4s3p2d1f] for nitrogen and a (15s9p2d1f) primitive set contracted to [5s4p2d1f] for sulfur. The CCSD(T) correlation energy was computed from a CCSD wavefunction with the effect of the linked triple excitations estimated perturbatively [16]. The quantum chemical calculations were performed using the MOLECULE [17–19] programs interfaced with TITAN [#1] that includes electron correlation through the MP2 and coupled cluster calculations.

The potential energy surface was obtained by a least-squares fit (using the singular value decomposition algorithm) of the discrete set of energy points at various distorted geometries. The experimental equilibrium geometry [2] was used as a reference geometry with a grid of distorted geometries generated by displacements of -0.3 to 0.4 a_0 for both the NN (r) and NS (R) bonds with a step size of 0.1 a_0 and 8° distortions of the linear angle bend (θ) with a maximum of 32°. In total, this represents 168 geometrically distinct energy points. Initially, both the CCSD and CCSD(T) surfaces were fitted to sextic valence expansions and later to sextic Morse coordinate expansions in the stretches [13,20,21]. The Morse exponential parameters for the NN and NS bonds, α_r and α_R, respectively, were obtained from non-linear one-dimensional fits. We note, however, that had we access to the appropriate analytic gradient codes, a considerably smaller number of points would have sufficed to obtain an accurate characterisation of the geometry and force constants.

The normal modes are labelled ω_1, ω_2 and ω_3, representing the NS stretch, the linear angle deformation and the NN stretch, respectively. Labelling of the anharmonic frequencies, ν_1, ν_2 and ν_3, also follows this convention. The band origins were first computed by second-order perturbation theory using the SPECTRO [22] program in conjunction with the quartic valence coordinate expansion. The variational vibrational band origins were calculated using the RVIB program [23,24] using the sextic Morse coordinate expansion. The vibrational basis set consisted of 51 stretch and 15 bend functions contracted from 256 primitive stretch functions (products of Morse oscillator functions) and 51 Legendre polynomials, respectively.

3. Results and discussion

The calculated equilibrium geometries and vibrational frequencies of N_2S are given in table 1 together with the corresponding experimental data. The predicted CCSD(T) NN bond length is in satisfactory agreement with experiment and it is very similar to the NN distance in N_2O [10]. However, the calculated NS bond lengths appear to be somewhat long. As the ab initio NO bond lengths in N_2O were significantly closer to experiment [10], it appears, despite the fact that N_2O and N_2S are isovalent, that the NS bond is a little more subtle and more difficult to describe than the NO bond. The most obvious difference is that in N_2S the potential energy surface is quite shallow with respect to the NS distance and consequently the energy is rather insensitive to variations in the NS bond length. It is possible that the sulfur basis may need to be larger, possibly containing *g* functions, for an accurate prediction of the NS distance. Unfortunately, computations with such a large basis are not feasible in our laboratories currently but such investigations of the basis set dependence of the geometry and potential energy are certainly worth considering.

The difference between the CCSD and CCSD(T) predictions is particularly evident in the case of the NN frequency, ω_3, where the difference is ≈ 125 cm^{-1}, indicating important contributions from the triple excitations; considerably larger than that observed in other multiply bonded species, viz. HCN [13] and N_2O [10]. To the best of our knowledge, the largest such effect to date has been noted for ozone where the triple excitations lower the harmonic antisymmetric stretch frequency by ≈ 250 cm^{-1} [12]. Comparison of the calculated band origins with experiment is complicated by the fact that most measurements to date have been carried out in Ar matrices. However, given the good agreement between the gas-phase and matrix values for

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[#1] T.J. Lee, A.P. Rendell and J.E. Rice, TITAN is a set of electronic structure programs.

Table 1
N_2S: equilibrium geometry, Morse exponents, harmonic frequencies and fundamental band origins

	CCSD	CCSD(T)	CCSD(T) [a]	Exp.
r_e(NN) (Å)	1.1167	1.1310	1.1320	1.1388 [b]
r_e(NS) (Å)	1.6080	1.5986	1.5910	1.5775 [b]
$\langle r(\mathrm{NN})\rangle$ [c] (Å)	1.1167	1.1314		
$\langle r(\mathrm{NS})\rangle$ [c] (Å)	1.6147	1.6046		
α_r ($\mathrm{Å}^{-1}$)		2.5083		
α_R ($\mathrm{Å}^{-1}$)		2.3949		
ω_1 (cm^{-1})	715.8	750.2	757	
ω_2 (cm^{-1})	471.1	464.9	469	
ω_3 (cm^{-1})	2217.0	2092.3	2080	
ν_1 (cm^{-1})	696.6	732.7		752 [d]
ν_2 (cm^{-1})	459.5	454.8		~343 [b]
ν_3 (cm^{-1})	2188.8	2063.0		2048 [b], 2039 [d], 2040 [e]

[a] Ref. [9]. [b] Ref. [2]. [c] Denotes vibrationally averaged distance.
[d] Ref. [4]. [e] Ref. [3].

the NN stretch frequency, ν_3, we may expect the NS stretch frequency, ν_1, measured in an Ar matrix, to be similarly close to the hypothetical gas-phase values, i.e. within ≈ 10 cm^{-1}. On the other hand, the bend frequency, ν_2, has been inferred from an analysis of the rotational band structure [2], rather than via direct observation.

For the stretches our anharmonic CCSD(T) band origins are within ≈ 20 cm^{-1} of the experimental values. Comparison of the corresponding harmonic frequencies, ω_1 and ω_3, with those of Collins et al. [9] shows reasonable agreement but also the sensitivity of these frequencies to the one-particle basis. Commenting on their CCSD(T) prediction of ω_3, Collins et al. [9] suggest that the anharmonic correction may be sufficient to bring the theoretical and experimental values of ν_3 into agreement. Although our best theoretical estimate of ν_3 is still ≈ 15 cm^{-1} too large, it is worth noting that applying our anharmonic correction of ≈ 30 cm^{-1} to the harmonic frequency of Collins et al. [9] yields a value of ≈ 2050 cm^{-1} which is in excellent agreement with experiment. With regard to the NS stretch frequency, we note that the calculated NS bond lengths are somewhat long when compared with experiment and this may have an adverse effect on the force field, especially on the NS frequency. Such effects have been examined in considerable detail in the recent study of Allen and Császár [25].

The largest discrepancy between theory and experiment occurs in the case of the bend: ≈ 100 cm^{-1}. In light of the good agreement in other systems such as HCN [13], N_2O [10] and O_3 [12], it is hard to believe that the calculations are in error by such a large margin, especially as the bend frequency in all these molecules has been consistently found to be very stable to variations in the level of correlation as well as in the one-particle basis. Nevertheless, we have considered the possibility that the (single reference) CCSD(T) calculations do not adequately resolve the effects of non-dynamic correlation, viz. orbital near-degeneracy, on the bending force constants. A measure of such effects is the $\mathcal{T}_1$ diagnostic of Lee and Taylor [26]. In N_2S, $\mathcal{T}_1$ is ≈ 0.02 and is effectively constant for bends up to $\approx 30°$ and is very similar to what has been observed in N_2O. Such a value of $\mathcal{T}_1$ is indeed indicative of the possibility of near-degeneracy problems, although, on the basis of the N_2O results, we would expect CCSD(T) to resolve these adequately. For comparison, in the case of O_3, $\mathcal{T}_1$ is ≈ 0.028 [12]. Nevertheless, as a final check, we carried out a complete active space SCF (CASSCF) [27] study of the bending potential in N_2S, using the MOLCAS programs [28]. The active space in these calculations consisted of the $2\pi_x$, $2\pi_y$,

$3\pi_x$ and $3\pi_y$ molecular orbitals among which four active π electrons are distributed. Thus, in addition to the (SCF) reference, $...9\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^2 2\pi_y^2$, configurations of the type $...9\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^2 3\pi_y^2$ and $...9\sigma^2 1\pi_x^2 1\pi_y^2 3\pi_x^2 2\pi_y^2$, etc. are introduced. The resulting wavefunctions, however, were found to be dominated by the SCF reference configuration (with a coefficient of 0.966) which were, moreover, fairly insensitive to the angle of the bend. The resulting CASSCF quadratic bending force constant (computed at the experimental geometry) is 0.514 aJ rad^{-1}, $\approx 20\%$ lower than the corresponding SCF value of 0.620 aJ rad^{-1}, but not very different from the MP2, CCSD and CCSD(T) values of 0.557, 0.579 and 0.568 aJ rad^{-1}, respectively. Additional dynamic correlation effects estimated by second-order multi-reference perturbation theory (using the CASPT2 program of MOLCAS [28]), increased the CASSCF bending force constant to 0.596 aJ rad^{-1}. Clearly, the correlated multi- and single-reference results are in reasonable agreement and the overall consistency in the predicted force constants is quite good. Given that the quartic and higher force constants have little effect on the fundamental frequency, an error of ≈ 100 cm^{-1} in the bending frequency corresponds to an error of over 50% in the quadratic force constant. It is most unlikely that the calculated values of that constant could be so poor. Thus, in this case, the validity of the experimental estimate of the bending frequency must be questioned.

The ab initio potential energy surfaces for N_2S is presented in two forms: as a quartic valence expansion of both the CCSD and CCSD(T) surfaces in table 2 and as the sextic Morse coordinate expansion of the CCSD(T) surface in table 3. The differences in the CCSD and CCSD(T) force fields are analogous to what has been observed for other small molecules [10,12,13], i.e. a significant change in the quadratic stretch terms whilst little difference is evident in the anharmonic terms. (As the bending force constants quoted in table 3 have been evaluated at the appropriate theoretical equilibrium geometries, they differ somewhat from those discussed earlier which were computed at the experimental geometry.)

The predicted vibrational band origins for N_2S, computed using both variational and perturbation methods, are listed in table 4 up to the first overtone in ν_3. Unfortunately, apart from the fundamental band origins listed in table 1, no other experimental frequencies are available to compare against. Nevertheless, the variational results, we hope, will facilitate assignment of the gas-phase spectrum in future experiments. At the same time, table 4 presents an interesting comparison between the perturbative and variational approaches in predicting and modelling anharmonic vibrational states and energies. As seen readily, the band origins obtained by perturbation theory are generally lower in energy than the variational results, the largest discrepancies noted for the ν_2 bending models, where the predicted fundamentals differ by 4.7 cm^{-1}. This discrepancy becomes progressively worse for higher bend overtones which is indicative of systematic errors that are propagated

Table 2
N_2S: CCSD and CCSD(T) quartic force constants in valence coordinates [a)]

	CCSD	CCSD(T)		CCSD	CCSD(T)
rr	20.55153	18.12379	*rrrr*	908.65278	857.27759
rR	1.43046	1.35886	*rrrR*	−7.75575	−9.74804
RR	4.54600	5.03598	*rrRR*	8.00463	7.57511
θθ	0.56537	0.55185	*rRRR*	−1.26093	1.91847
rrr	−150.09291	−136.13965	*RRRR*	181.06922	183.28263
rrR	−1.44879	−2.67247	*rrθθ*	−0.49776	0.38594
rRR	−1.72974	−0.64489	*rRθθ*	2.18784	2.17442
RRR	−34.60284	−36.47485	*RRθθ*	1.67706	1.55518
rθθ	−0.86216	−0.91279	*θθθθ*	0.87975	1.23233
Rθθ	−1.21128	−1.14546			

[a)] Units are consistent with energy in aJ, lengths in Å and angles in rad.

Table 3
N_2S: CCSD(T) potential energy surface in Morse coordinates a)

i	*j*	*k*	C_{ijk}	*i*	*j*	*k*	C_{ijk}	*i*	*j*	*k*	C_{ijk}
2	0	0	0.3294661	1	1	2	0.0423036	5	1	0	0.0376748
1	1	0	0.0518148	0	2	2	−0.0119918	4	2	0	−0.0005752
0	2	0	0.1007154	0	0	4	0.0093586	3	3	0	0.0038618
0	0	2	0.0635843	5	0	0	−0.0313214	2	4	0	0.0246333
3	0	0	0.0079141	4	1	0	0.0127164	1	5	0	−0.0056169
2	1	0	0.0027607	3	2	0	−0.0026386	0	6	0	−0.0219738
1	2	0	0.0202529	2	3	0	0.0259359	4	0	2	−0.1064330
0	3	0	−0.0015555	1	4	0	0.0032423	3	1	2	0.0286553
1	0	2	−0.0388577	0	5	0	−0.0087711	2	2	2	0.0146191
0	1	2	−0.0551984	3	0	2	−0.0549051	1	3	2	−0.0013821
4	0	0	0.0261144	2	1	2	0.0302013	0	4	2	0.0004297
3	1	0	−0.0157946	1	2	2	0.0104141	2	0	4	−0.0266319
2	2	0	0.0111160	0	3	2	−0.0027292	1	1	4	0.0081334
1	3	0	0.0142618	1	0	4	−0.0025946	0	2	4	−0.0027217
0	4	0	−0.0037954	0	1	4	−0.0107424	0	0	6	0.0049182
2	0	2	−0.0135070	6	0	0	−0.0711510				

a) Potential is expressed as $V(y_r, y_R, \Delta\theta) = \sum_{i,j,k} C_{ijk} y_r^i y_R^j \Delta\theta^k$ where y_r and y_R denote the Morse coordinates for the NN and NS bonds, respectively. Morse exponents used: $\alpha_r = 1.32735\ a_0^{-1}$ and $\alpha_R = 1.26734\ a_0^{-1}$. In au.

Table 4
N_2S: Vibrational band origins from perturbation theory and variational method a)

	Variational		Perturb. valence d)		Variational		Perturb. valence d)
	Morse b)	valence c)			Morse b)	valence c)	
$0\,1^1\,0$	459.5	460.1	454.8	$1\,5^1\,0$	3000.0	3004.1	2940.0
$1\,0^0\,0$	732.0	732.8	731.8	$3\,2^0\,0$	3039.8	3053.7	3023.0
$0\,2^0\,0$	919.3	920.2	904.3	$0\,7^1\,0$	3208.7	3211.8	3103.3
$1\,1^1\,0$	1186.4	1188.0	1181.2	$1\,1^1\,1$	3243.4	3249.6	3241.8
$0\,3^1\,0$	1378.5	1379.7	1351.9	$2\,4^0\,0$	3243.7	3252.2	3200.5
$2\,0^0\,0$	1449.0	1452.7	1448.6	$4\,1^1\,0$	3279.4	3303.9	3271.0
$1\,2^0\,0$	1640.7	1642.8	1625.5	$0\,3^1\,1$	3423.8	3429.2	3396.6
$0\,4^0\,0$	1837.3	1838.8	1794.3	$1\,6^0\,0$	3451.2	3456.4	3370.0
$2\,1^1\,0$	1898.6	1903.4	1892.8	$3\,3^1\,0$	3483.3	3499.3	3454.7
$0\,0^0\,1$	2062.0	2065.3	2063.0	$2\,0^0\,1$	3496.4	3518.6	3518.9
$1\,3^1\,0$	2094.5	2097.2	2067.8	$5\,0^0\,0$	3527.5	3556.4	3509.3
$3\,0^0\,0$	2150.9	2161.3	2150.5	$0\,8^0\,0$	3663.6	3667.7	3531.3
$0\,5^1\,0$	2295.3	2297.2	2234.7	$2\,5^1\,0$	3690.6	3700.6	3630.4
$2\,2^0\,0$	2347.6	2353.5	2331.7	$1\,2^0\,1$	3691.1	3698.9	3679.9
$0\,1^1\,1$	2515.6	2519.7	2511.7	$4\,2^0\,0$	3719.3	3746.2	3699.3
$1\,4^0\,0$	2547.6	2550.9	2504.9	$0\,4^0\,1$	3877.7	3883.9	3832.9
$3\,1^1\,0$	2595.9	2607.9	2589.3	$1\,7^1\,0$	3901.5	3908.0	3798.0
$0\,6^0\,0$	2752.5	2754.9	2670.0	$3\,4^0\,0$	3925.5	3944.1	3881.2
$1\,0^0\,1$	2795.4	2800.3	2798.4	$2\,1^1\,1$	3933.8	3962.3	3957.0
$2\,3^1\,0$	2796.2	2803.2	2768.7	$5\,1^1\,0$	3969.4	3996.9	3937.6
$4\,0^0\,0$	2838.5	2860.9	2837.4	$0\,0^0\,2$	4099.1	4110.7	4100.7
$0\,2^0\,1$	2970.0	2974.7	2955.1				

a) All potentials used derive from the cc-pVTZ CCSD(T) discrete potential. In units of cm^{-1}.

b) Derived from sextic Morse coordinate expansion. Ground state energy: 1876.1 cm^{-1}.

c) Derived from quartic valence coordinate expansion. Ground state energy: 1878.2 cm^{-1}.

d) Derived from quartic normal coordinate expansion (transformed from the quartic valence coordinate expansion). Ground state energy: 1874.8 cm^{-1}.

and amplified. Two possible sources of error, viz. basis set incompleteness in the variational calculations and truncation of the valence potential to quartic terms in the perturbative calculations have been ruled out by test calculations. With regard to basis set incompleteness, test calculations using incrementally larger numbers of bend basis functions have indicated that the results in table 4 are essentially converged with respect to the size of the basis. If truncation of the potential was responsible this should be reflected in the third column of table 4 where the quartic valence potential used in the variational calculations is identical to the one used in the perturbation calculations. However, the resulting band origins are *higher* in energy than those obtained using the Morse expansion and therefore, in even greater contrast with the lower lying the perturbation results. There are two remaining effects that are related and cannot be readily separated. The first is the effect of the non-linear transformation from a valence coordinate representation of the potential to the normal coordinate representation. The resulting potential truncated at quartic terms may not accurately represent the original potential in valence coordinates. The second is the finite order of the perturbation calculation. In a second-order treatment, the zeroth-order states are coupled only directly, i.e. to first order, although in some cases the effect of the indirect couplings (e.g. via a third intermediate state) may well be important. This fundamental shortcoming in the perturbation method is well appreciated although little quantitative information on this point in the context of vibrational energies is available. The reason why these two effects cannot be separated is that even if the normal coordinate expansion was lengthened such that it accurately resembled the valence potential, the second-order treatment does not include potential terms that are higher than quartic. We note also that the bend overtone frequency, $2\omega_2$, is too large to be considered in Fermi resonance with the NS stretch, ω_1 (unlike N_2O).

4. Conclusion

In this Letter, we presented a potential energy surface of N_2S, calculated using the CCSD(T) method in conjunction with a cc-pVTZ basis set. The predicted harmonic frequencies are in much better agreement with experiment than the early theoretical studies [4–8]. More importantly though, this study has provided a theoretical prediction of the anharmonic frequencies which are needed for a proper comparison to be made with the experimental data. We have also predicted overtone and combination bands up to ≈ 4100 cm^{-1} using our ab initio potential in a variational calculation of the vibrational states, which may aid future spectroscopic studies of N_2S.

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