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Theoretical study of ^{14}N quadrupole coupling constants in some NO-containing complexes: N_2O_3 and FNO

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ABSTRACT

The nuclear quadrupole coupling constants at nitrogen centers have been computed for N_2O_3 and FNO by employing the complete-active-space self-consistent field, internally contracted multireference configuration interaction and single-configuration coupled-cluster methods with correlation-consistent basis sets at the levels of attainable accuracy. To examine the overall quality of the wave functions used in our calculations, also electric dipole moments and potential energy characteristics were calculated and compared with available experimental and recent theoretical data. The effects of the choice of the basis set and reference configuration space were investigated. The robust changes in the electric field gradients occurring in the course of complex formation from isolated subunits were interpreted in terms of wave function composition. Our calculations confirm the assignment of the ^{14}N nuclear quadrupole coupling constants to nuclear centers in N_2O_3 provided by the microwave measurements of Cox et al. [A.P. Cox, J. Randell, A.C. Legon, Chem. Phys. Lett. 126 (1986) 481.].

1. Introduction

In our previous work [2] an investigation of the electric field gradients (EFGs) at nitrogen nuclei in the nitric oxide dimer $(NO)_2$ and its singly charged ions at the complete-active-space self-consistent field (CASSCF) level was carried out. The theoretical ^{14}N quadrupole coupling constant in $(NO)_2$ was determined and changes in the electric field gradients due to the complex formation from NO subunits [3] were used to interpret the character of bonding in the dimers. From the theoretical point of view, NO ($^2\Pi$) is an interesting subunit inside complexes, because perturbation due to complex formation is lifting degeneracy, leading to closely spaced energy levels at weak interaction of subunits and, therefore, requiring highly demanding computations.

In this paper we turn our attention to dinitrogen trioxide and nitrosyl fluoride which provide further cases of EFG modification in NO resulting from the approach of an other subunit, and simultaneously offer an opportunity to render theoretical values for the respective ^{14}N QCCs. The first microwave spectroscopic studies of N_2O_3 [4] and FNO [5], furnishing both structure parameters and nuclear quadrupole coupling constants (NQCCs), were reported almost forty years ago in the same issue of a journal. Since then a number of experimental and theoretical studies appeared on N_2O_3 [6–13] and FNO [14–19] (and references therein) devoted to the interpretation and determination of structures, spectroscopic properties, dipole moments, heats of formation, etc., including those providing new ^{14}N QCCs on the basis of high-resolution measurements [1,20], and henceforth values of the electric field gradient (EFG) at nitrogen sites in N_2O_3. A theoretical investigation of the EFGs in N_2O_3 is all the more desirable, because of the encountered problems with the analysis of the complex experimental hyperfine structure of rotational spectra arising from two non-equivalent nuclei [1,20] leading to the original misassignment of the two sets of ^{14}N coupling constants.

2. Computational details

The calculations on the title species were performed using the CASSCF [21,22] method with a possibly ensuing internally contracted multireference configuration interaction (icMRCI) procedure [23,24], and the single-configuration (spin-restricted (R)) coupled-cluster approach including single, double and a perturbative estimate of triple excitations (CCSD(T) or RCCSD(T)) [25–27]. Several correlation-consistent polarized valence (cc-pVXZ, X = D, T, Q) basis sets of Dunning and coworkers, including augmented (aug) and core-valence (pCVXZ, wCVXZ) versions [28–31], were used.

The quantum-chemical computations were carried out using the MOLPRO (version 2002.6) suite of programs [32], ACES II [33] and DALTON [34] electronic structure program packages. In more detail, MOLPRO was employed in applying the CASSCF/icMRCI

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method to the calculation of the expectation values of the traceless Born–Oppenheimer EFG tensor at the nucleus A, $\boldsymbol{q}^{A}$, the electric dipole moment μ, and in using the CASSCF/icMRCI and CCSD(T) methods for geometry optimization and harmonic vibrational frequency determination. Because calculations of the first-order physical properties are not available for all these methods with the MOLPRO suite of programs, CCSD(T) EFGs and dipole moments were computed with the ACES II program package. The DALTON suite of programs was used to check selected EFG results of MOLPRO calculations at the MCSCF level of theory.

The NQC tensor $\boldsymbol{\chi}^{A}$ is related to the EFG by $\chi^{A}_{ab} = eQq^{A}_{ab}$ [35], where e is the elementary electric charge and Q the effective electric quadrupole moment at the nucleus A, with Q (^{14}N) taken to be 0.02044 *b* [36]. Correspondingly, the ^{14}N QCC value in MHz is obtained by multiplying the EFG/a.u. by −4.802678.

In the CCSD(T) optimization calculations, the number of core orbitals was set equal to the number of inner (1s) orbitals. In regard to the CCSD(T) approach applied to the EFG calculations, all electrons have been correlated. Concerning the CASSCF calculations, different types of active spaces (ASs) had to be used for three- and five-atomic species. While calculations on FNO (and NO_2) could be performed at the "standard" full valence AS (or even with an extended AS by including the 1s-like core orbitals), in treating N_2O_3 limitations had to be implied on the AS by fixing the number of occupied orbitals to 11 (exceptionally to 10) which - though optimized – were constrained to doubly occupation. The reason for these restrictions lies in the sizable dimension of the ASs which for the symmetry- and spin-adapted $^1A'$ state of N_2O_3 leads to 1,074,585 and 2,864,950 configuration state functions, respectively. The respective ASs consist of 14 active orbitals with 16 active electrons, and of 15 active orbitals with 18 electrons, denoted in Tables 2 and 3 by short-hand notation as (16, 14) and (18, 15), respectively. Thus, in CASSCF calculations on N_2O_3 no core correlation phenomena have been included, and from the use of core-valence basis sets no significant effects could be expected.

The vibrational corrections to the electric properties were ignored in our estimates on grounds that the procedures for their evaluation are highly computer-time consuming, and that the zero-point corrections were found to be negligible for the ^{14}N quadrupole coupling constants in systems similar to ours [37–39]. Geometry optimization and harmonic vibrational frequency calculations were performed using the "no symmetry" option giving rise to a further increase in the dimensionality of calculations.

Although energy optimization has not been the main goal of this study (and for example, no stabilization energies of the complexes have been calculated), results on the Born–Oppenheimer equilibrium structure are also reported, in order to assess the quality of the basis sets and the methods used in this investigation, and to aid comparison with previous work on given systems. For the same reason, expectation values of the electric dipole moments were calculated. Calculations for the molecules have been carried out not only at optimized geometries, but also at experimental geometries to guarantee comparison with experimental investigations published in the literature. In order to properly compare and discuss our results on N_2O_3 and ONF, the EFG components and the atomic orbitals will be presented in molecular coordinate systems indicated in Figs. 1 and 2 which show the structure of the molecules and the orientation of the inertial axis systems.

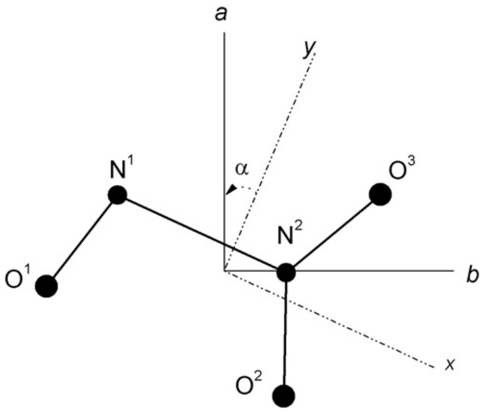

Fig. 1. Coordinate systems used to characterize the geometry of N_2O_3 (α = 23.91° for the structure defined in [4]).

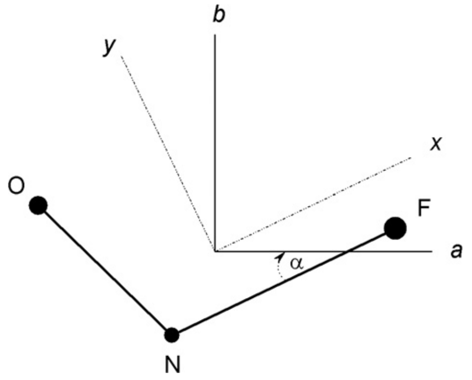

Fig. 2. Coordinate systems used to characterize the geometry of FNO (α = 25.61° for the structure defined in [5]).

3. Results and discussion

3.1. N_2O_3

Structural parameters and harmonic vibrational frequencies calculated using single-reference CCSD(T) and CASSCF methods for the most stable asymmetric (C_s) geometric arrangement are given in Tables 1 and 2 together with results from the literature. This isomer is responsible [4] for the observed microwave spectrum associated with the ^{14}N quadrupole coupling constants. While the calculated N–O bond lengths and bond angles agree fairly well with the values corresponding to the experimental structures, the N–N length is at the CCSD(T)/cc-pVTZ level of theory underestimated by about 0.03 Å, and with the CASSCF method about twice as much. Interestingly, our results lie closer to theoretical values based on a density functional formalism [9] than on MP2 calculations [10], and well comparable with those identified as "best *ab initio*" [13], as seen in Table 1. As far as the vibrational frequencies in Table 2 are concerned, our results are in good agreement with the infrared measurements in gas phase [6] combined with Raman data [7], and support the suggestion of Stirling et al. [9] for a reverse assignment of the bands close to 630 and 410 cm^{-1}.

For the energetically higher-lying symmetric (C_{2v}) W-shaped isomer (O^2–N^1–O^1–N^2–O^3) we obtained with the CCSD(T) method using the cc-pVTZ basis set: $R(N^1O^2) = 1.1658$ Å, $R(N^1O^1) = 1.4798$ Å, $\angle O^1N^1O^2 = 109.69°$ and $\angle N^1O^1N^2 = 103.26°$ which agrees quite well with the MP2 values of Wang et al. [10], however differs in that our optimization procedure provides a "fully" C_{2v} symmetric structure, and not a slightly distorted one as presented in Table 1 of [10].

Up to the computational level for us practicable, the results of our CASSCF EFG calculations on N_2O_3 and its subunits are summarized in Table 3, in accordance with the orientation of the molecule in the Cartesian coordinate system fixed in space introduced in Fig. 1. The CASSCF approach enables an effective treatment of multiconfiguration effects in the whole range of interunit separation,