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Computational spectroscopy of NCS in the Renner-degenerate electronic state $\widetilde{X}\,^2\Pi$

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ABSTRACT

$\widetilde{X}\,^2\Pi$ NCS is a Renner-degenerate linear molecule. Based on three-dimensional potential energy surfaces and dipole moment surfaces computed *ab initio* for NCS in the $\widetilde{X}\,^2\Pi$ electronic ground state at the core-valence, full-valence MR-SDCI+Q/[aug-cc-pCVQZ(N, C, S)] level of theory, we have calculated values of the ro-vibronic energies, intensities, and rotational constants. All values obtained are in good agreement with the available experimental data. Ro-vibronic spectra are also simulated in RENNER calculations.

1. Introduction

When, for a chain molecule, the electronic state is degenerate at linear configurations (that is, when the electronic angular momentum $\Lambda \geqslant 1$), the degenerate state will split into two nondegenerate states as the molecule bends out of linearity. There are generally non-negligible interactions between the rovibronic states associated with these two electronic states and in calculations of the rovibronic energies and wavefunctions, the two electronic states must be considered together. The effect of the interactions on the rovibronic states is called the Renner (or Renner-Teller) effect [1]. The Renner effect is most prominent in Π ($\Lambda = 1$) electronic states [2] and almost negligible for states with a higher electronic angular momentum ($\Lambda > 1$), i.e., $\Delta, \Phi, \Gamma, \ldots$ states. See, for example, Refs. [2–4] for discussions of the Renner effect in the context of high-resolution molecular spectroscopy.

The electronic ground state of the NCS radical is $^2\Pi$, and so it is Renner-degenerate just as the electronic ground states of the other 15-valence-electron triatomics BO_2, N_2O^+, and NCO. At linear geometries, the electronic ground state of NCS is doubly degenerate with Π symmetry, but it splits into two separate states upon bending. Because of the Renner interaction in $\widetilde{X}\,^2\Pi$ NCS and of the facts (1) that $2\omega_2 \approx \omega_3$, leading to all-pervading Fermi resonances, and (2) that the spin-orbit coupling constant is close in size to ω_2, the resulting rovibronic spectrum is extremely complicated. This spectrum was first observed by Dixon and Ramsay [5] in 1968 with more recent experimental studies from Northrup and Sears [6–8], Tokue et al. [9], Amano and Amano [10], McCarthy et al. [11], and Maeda et al. [12]. Owing to the complications just mentioned, the rovibronic spectrum of NCS has been experimentally characterized to a much lesser extent than that of the sister molecule NCO which is known as one of the prototype Renner molecules. NCS is of astrochemical interest, since the HNCS molecule is observed toward Sgr B2 [13,14] and TMC-1 [14] and this molecule is known to yield NCS by photolysis [15].

Several *ab initio* calculations have been reported for NCS, including those of Koch and Frenking [16], Tokue et al. [9], Li and Iwata [17], the Szalay group [18,19], and Ouazbir et al. [20]. However, these calculations were unable to reproduce the experimental B_0 values with the accuracy required for the theoretical results to be useful in assisting the assignment of experimental spectra and the identification of molecules in remote-sensing experiments, for example of interstellar space.

In 2003, we found that the core-valence correlation in MR-SDCI +Q-level calculations improved dramatically the agreement with experiment for the rotational constant B_0. The experimentally derived B_0 values of NCS and $NC^{34}S$ reported by Maeda et al. [12] were reproduced with deviations of −0.03% and −0.04%,

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respectively [21]. These two-dimensional (2D) calculations in terms of the N–C and C–S bond-lengths are extended here to produce the full three-dimensional (3D) potential energy surfaces (PESs).

In the present work we first generate 3D *ab initio* PESs at the core-valence, full-valence MR-SDCI+*Q*/[aug-cc-pCVQZ(S, C, N)] level of theory and, based on these PESs, we calculate the ro-vibronic energies and intensities with the RENNER program system [4,22–24] and simulate ro-vibrational spectra.

Electronic properties, molecular constants, ro-vibrationally averaged strucures etc. is reported elsewhere [25].

2. *Ab initio* calculations

The 3D PES and dipole-moment surface calculations were carried out under $\mathbf{C}_s$ symmetry constraint at the level of core-valence, full-valence MR-SDCI+*Q*/[aug-cc-pCVQZ(S, C, N)]. For details of the calculations see Ref. [25].

The $\tilde{X}\,^2\Pi$ NCS molecule has its potential minima at the linear configuration. Hence, in spectroscopic terminology, it is a linear molecule. Fig. 1 shows the bending potential energy function along the minimum energy path (MEP) obtained by optimizing the internuclear distances (so as to minimize the energy) at given values of $\bar{\rho} = 180° - \angle$(N–C–S). It is seen that the $^2\Pi$ doubly degenerate bending potential splits into A' and A'' states as the molecule bends.

The equilibrium structure has r_e(N–C) = 1.1778 Å, r_e(C–S) = 1.6335 Å, and $\angle_e$(N–C–S) = 180°. The Renner parameter ϵ $((\omega_{2A'})^2 - (\omega_{2A''})^2)/((\omega_{2A'})^2 + (\omega_{2A''})^2)$, associated with a perturbation treatment of the Renner effect, is −0.1653. The spin-orbit coupling constant $A_{so} = -342.2\ \mathrm{cm}^{-1}$, and the unpaired electron resides almost entirely on the S nucleus. The dipole moment value at the equilibrium structure, calculated as the finite electric field derivative of the core-valence, full-valence MR-SDCI+*Q*/[aug-cc-pCVQZ (S, C, N)] energy, is 2.52 D, with the N end of the molecule being negatively charged. The Yamada-Winnewisser quasi-linearity parameter [26] γ_0 is calculated to be −1.05, a value indicating a linear molecule.

3. The RENNER program system

The RENNER program system [4,22–24] computes the rovibronic energies for a triatomic molecule in a Renner-degenerate electronic state, taking into account the spin-orbit interaction.

3.1. Coordinates

As coordinates for the vibrational motion, the RENNER approach uses r_{12}, r_{32}, and $\bar{\rho}$; they are shown in Fig. 2. Here, r_{12} and r_{32} are the instantaneous values of the C–N and C–S distances, respectively, and as already mentioned $\bar{\rho} = 180° - \angle$(N–C–S).

The dipole moment and the transition dipole moment are described by means of the axis system (x, q, p) (Fig. 2). The origin of the (x, q, p) axis system is in the nuclear center of mass of the molecule. The p axis is parallel to the C-S bond, pointing toward the S nucleus. The q axis is perpendicular to the p axis and is directed so that the q coordinate of the N nucleus is positive.

3.2. The RENNER calculation

When NCS bends out of the linear equilibrium configuration, the electronic energy of the $\tilde{X}\,^2\Pi$ state splits into two non-degenerate components $1\,^2A'$ and $1\,^2A''$ (see Fig. 1). The two corresponding potential energy functions are denoted as $V_-(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho})$ and $V_+(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho})$, respectively, and we

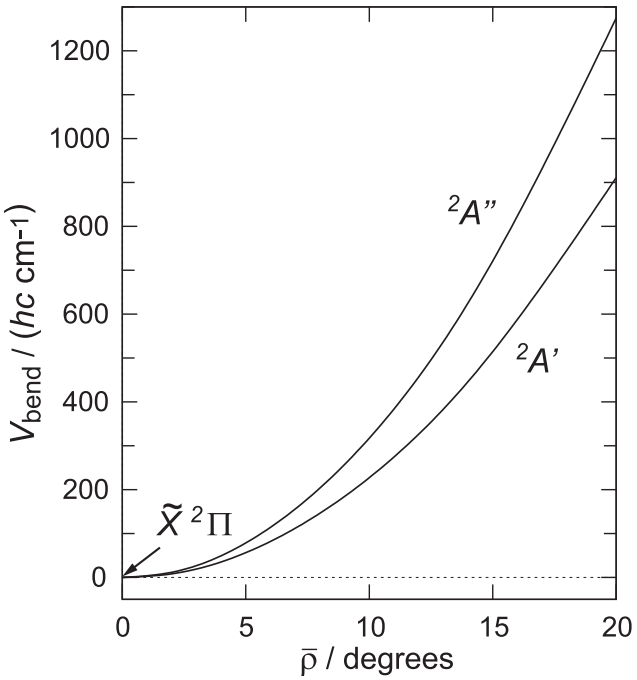

Fig. 1. The potential energy V_{bend} along the bending minimum energy path (MEP) for $\tilde{X}\,^2\Pi$ NCS, calculated at the core-valence, full-valence MR-SDCI+*Q*/[aug-cc-pCVQZ(S, C, N)] level of theory. The energy is plotted against $\bar{\rho} = 180° - \angle$(N-C-S).

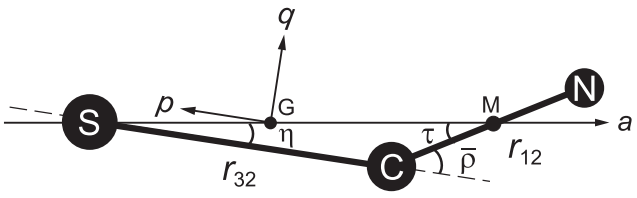

Fig. 2. The definitions of the angles $\bar{\rho}, \tau$, and η used to describe the geometry of the NCS molecule. The axis labeled '*a*' passes through the S nucleus and through M, the center of mass of the CN moiety. This axis is not identical, but very close, to the *a* principal axis of the molecule. G is the center of mass of the complete molecule.

represent them by the following analytical functions (see Refs. [4,22–24])

$$V_{\pm}(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho}) = \sum_{jkl} G_{jkl}^{(\pm)} \left(y_1^{(\mathrm{ref})}\right)^j \left(y_3^{(\mathrm{ref})}\right)^k (1 - \cos\bar{\rho})^l \qquad (1)$$

where the '−'('+') refers to the lower(upper) component $1\,^2A'$ ($1\,^2A''$), and $G_{jkl}^{(\pm)}$ are expansion coefficients. We have

$$y_i^{(\mathrm{ref})} = 1 - \exp(-a_i \Delta r_{i2}^{(\mathrm{ref})}) \qquad (2)$$

where i = 1 or 3. The function $y_1^{(\mathrm{ref})}$ is associated with the C–N bond, whereas $y_3^{(\mathrm{ref})}$ is associated with the S–C bond. The two functions are expressed in terms of the molecular constants a_i and the displacement $\Delta r_{i2}^{(\mathrm{ref})} = r_{i2} - r_{i2}^{(\mathrm{ref})}$ of the instantaneous internuclear distance r_{i2} from its reference value $r_{i2}^{(\mathrm{ref})}$. In the present work, we choose for each bond length $r_{i2}^{(\mathrm{ref})} = r_{i2}^{\mathrm{e}}$ with r_{i2}^{e} as the equilibrium value of r_{i2} which, for NCS, is common for the two potential energy surfaces. Note that in Eq. (1), the parameters $G_{jk0}^{(+)} = G_{jk0}^{(-)}$; this ensures that the two functions $V_-(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho})$ and $V_+(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho})$ are degenerate at linear configurations where $\bar{\rho} = 0$.

Table 1 shows the values of the parameters obtained in a least squares fitting of the functions $V_{\pm}(\Delta r_{12}^{(\mathrm{ref})}, \Delta r_{32}^{(\mathrm{ref})}, \bar{\rho})$ in Eq. (1) to