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High-level theoretical rovibrational spectroscopy of HCS^+ isotopologues

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ABSTRACT

In this work the rovibrational spectrum of the HCS^+ molecular cation is revisited through high-level electronic structure and variational rovibrational calculations. A local potential energy function is built from explicitly correlated coupled-cluster results, incorporating corrections for core-valence, scalar relativistic and higher-order excitation effects. The computed spectroscopic parameters, based on variational calculations with Watson's isomorphic Hamiltonian for linear molecules lead to a nearly perfect agreement with experimentally reported values (Rosenbaum et al., 1989). Furthermore, the documented Fermi resonance within the $(0,0^0,1)/(0,2^0,0)$ and $(1,0^0,1)/(1,2^0,0)$ pairs of states is clarified. Based on a newly developed electric dipole moment function transition dipole moments of fundamental transitions are predicted for the most important isotopologues.

1. Introduction

The thioformyl cation HCS^+ ($X^1\Sigma^+$) was first detected in the interstellar medium by Thaddeus et al. [1] in 1981. Four harmonically related emission lines in the microwave region were observed toward various sources. The tentative assignment to HCS^+ was based on a comparison of the ground state rotational constant B_0 to an *ab initio* value reported years earlier by Wilson [2]. This assignment was immediately confirmed by laboratory studies when Woods and coworkers [3] observed the rotational transition from $J = 1$ to $J = 2$ where J is the rotational quantum number. Very recently the first secure detection of DCS^+ toward the dark cloud Barnard B1b was reported by Fuente et al. [4] using the IRAM 30-m telescope.

The spectrum of HCS^+ both in the microwave and infrared has been investigated by high-resolution spectroscopy. Bogey et al. [5] extended the observed rotational spectrum to the millimeter wave region including transitions up to $J = 7$. One year later, Davies and Rothwell [6] reported the first measurement of the ν_2 fundamental (bend) by diode laser spectroscopy. Guided by the *ab initio* calculations of Botschwina and Sebald [7] the experimental band origin was determined to be $766.4529(10)\,\mathrm{cm}^{-1}$ with the error corresponding to three standard deviations (3σ) given in parentheses. Shortly afterwards, Saykally and coworkers [8] observed the ν_1 band (CH stretch) of HCS^+ at $3141.6323(5)\,\mathrm{cm}^{-1}$ using velocity modulation color center laser spectroscopy. Rosenbaum et al. [9] extended their earlier measurements of the HCS^+ spectrum in the ν_1 region in 1989. They assigned four hot bands originating from excited bending vibrational states and from the first excited CS stretching state (ν_3). Rosenbaum et al. [9] discussed and analyzed a Fermi resonance within the experimentally observed pairs of states $(0,0^0,1)/(0,2^0,0)$ and $(1,0^0,1)/(1,2^0,0)$. This seems reasonable since Botschwina and Sebald [7] predicted the ν_3 fundamental band around $1410\,\mathrm{cm}^{-1}$ and the ν_2 band around $740\,\mathrm{cm}^{-1}$. These values suggest a separation of the (0,0,1) and (0,2,0) states by only about $70\,\mathrm{cm}^{-1}$. Furthermore, Rosenbaum et al. [9] found a local perturbation in the $(1,0^0,1)$ state near $J = 28$ and identified with some evidence the $(0,6^2,0)$ state as the perturbing state.

The rotational spectra of the less abundant isotopologues $D^{12}C^{32}S^+$, $H^{13}C^{32}S^+$ and $H^{12}C^{34}S^+$ together with the main isotopologue were first investigated by Tang and Saito [10] and later extended up to 1 THz by Margulès et al. [11]. The latter were able to determine estimates for the sextic centrifugal distortion constant in the vibrational ground state (H_0). Margulès et al. [11] also determined a mixed experimental/theoretical equilibrium geometry for the thioformyl ion. Rotation-vibration coupling constants obtained from frozen core (fc) CCSD(T)/cc-pVQZ calculations were combined with the experimental rotational constants for the above mentioned isotopologues. The resulting equilibrium structure is $r_e(\mathrm{HC}) = 1.080686(13)$ Å and $R_e(\mathrm{CS}) = 1.475869(3)$ Å. The uncertainties quoted in parentheses were solely determined from the fit of the rotational constants.

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As shown in the preceding discussion, *ab initio* calculations have closely followed the experimental studies on HCS^+ providing crucial information for band assignment and overall spectra interpretation. In their seminal paper Botschwina and Sebald [7] provided a thorough investigation on the spectroscopic properties of HCS^+. Based on coupled electron pair approximation (CEPA) calculations in a basis of 80 contracted Gaussian-type orbitals (cGTOs) they developed a two dimensional stretch-only potential energy function (PEF) as well as a stretch-only electric dipole moment function (EDMF). The PEF was further refined by adjusting the CS bond length and scaling the R dependent part with corrections obtained from similar calculations on diatomic CS. Stretching vibrational frequencies were then obtained variationally using an approximate stretch-only Hamiltonian that takes the stretch-bend coupling parametrically into account. The resulting stretching vibrational frequencies were $\nu_1 = 3154 \pm 5\ \mathrm{cm}^{-1}$ and $\nu_3 = 1410 \pm 5\ \mathrm{cm}^{-1}$, the former in remarkable agreement with the then unknown experimental value considering the employed level of theory. Additionally, Botschwina and Sebald predicted the bending fundamental at $\nu_2 = 739 \pm 10\ \mathrm{cm}^{-1}$ somewhat lower than the experimental value due to the limited basis set size used in the *ab initio* calculations.

The most recent theoretical study on HCS^+ was carried out by Puzzarini [12]. Spectroscopic parameters for HCS^+ were calculated by second order vibrational perturbation theory in normal coordinate space (VPT2). The PEF was based on large scale coupled cluster calculations that take the effect of inner shell correlation and scalar relativistic effects into account. Puzzarini [12] calculated the composite harmonic vibrational frequencies (although quoted as ν_i typically used for anharmonic values) to be $3272.3\ \mathrm{cm}^{-1}$, $783.5\ \mathrm{cm}^{-1}$ and $1427.6\ \mathrm{cm}^{-1}$ for ω_1, ω_2 and ω_3, respectively. Furthermore, a ground state rotational constant of $B_0 = 21351.6$ MHz was calculated based on the composite results. The latter value differs from the accurate experimental value [11] by 14.5 MHz or 0.07%.

Despite its importance in astrochemistry [1,4,10] no full 3D PEF and EDMF is available for the HCS^+ molecular cation. It is the purpose of this contribution to fill this gap. To this end, a high-level *ab initio* composite approach is employed in the construction of the PEF. Variational calculations employing the composite PEF then provide vibrational band origins with an accuracy of $1\ \mathrm{cm}^{-1}$. Such composite methods have become increasingly popular in the past few years (see, e.g. [13] for a review). Recent *ab initio* studies based on the present approach dealt with the neutral triatomic molecules CO_2 [14], N_2O [15] and C_3 [16] as well as the ionic species N_3^- [14], HBF^+ [17], NO_2^+ [18] and CNC^+ [19].

2. Methods

2.1. Electronic structure calculations

Unless otherwise noted all electronic structure calculations of the present work are carried out with the MOLPRO package of *ab initio* programs [20] with an interface to Kállay's MRCC program [21]. The construction of the PEF follows a well established composite procedure [14–19]. Briefly, the potential energy function is obtained as the sum of individual contributions:

1. The basic contribution is calculated at the fc-CCSD(T)-F12b level of theory [22–24] (abbreviated F12b). The F12-optimized basis set cc-pVQZ-F12 [25] (VQZ-F12) is employed as atomic orbital (AO) basis with a geminal parameter of $\beta = 1.0\ a_0^{-1}$. As auxiliary basis sets necessary for F12-calculations VQZ-F12/OPTRI [26], VQZ/JKFIT [27] and AVQZ/MP2FIT [28] are employed. The quality of the F12b/VQZ-F12 contribution is checked by comparison to standard fc-CCSD(T) calculations employing large Dunning style [29] AO basis sets.
2. The second contribution (termed CV) accounts for the effect of core-core and core-valence correlation. Standard CCSD(T) calculations are performed employing the large cc-pCV6Z basis set (596 cGTOs). The CV contribution is then obtained as energy difference between the result of all electron and frozen core calculations.
3. Scalar relativistic effects (SR) are considered by means of fc-CCSD(T) calculations employing the 2nd order Douglas-Kroll-Hess (DKH2) hamiltonian [30,31]. The SR contribution is calculated as energy difference of calculations with and without the DKH2 hamiltonian. While a recontracted cc-pVQZ-DK basis set [32] is employed in the DKH2 calculations, the calculations without the DKH2 hamiltonian use the standard cc-pVQZ basis set.
4. Higher-order correlation effects (HC) beyond fc-CCSD(T) are included through three individual contributions which are calculated as energy differences. The first and most important contribution termed (Q)-(T) is obtained from CCSDT(Q) [33,34] and CCSD(T) calculations using the cc-pVTZ basis set. A second contribution denoted Q-(Q) is calculated at the CCSDTQ [35] and CCSDT(Q) level with the smaller cc-pVDZ basis set. Finally we include the effect of pentuple excitations through CCSDTQP [35] and CCSDTQ calculations (abbreviated P-Q) also with the cc-pVDZ basis set.
5. Effects beyond the Born-Oppenheimer approximation are included by means of the diagonal Born-Oppenheimer Correction (DBOC). The DBOC contribution is calculated at the all electron CCSD level of theory [36] with the cc-pCVQZ basis set. The calculations are carried out with the CFOUR program package [37].

The mixed experimental/theoretical geometry of Marguls et al. [11] $r_{\mathrm{ref}} = 1.0807$ Å and $R_{\mathrm{ref}} = 1.4759$ Å is used as common reference geometry in the calculations of all contributions. Calculations around the reference structures are carried out in the ranges $-0.225\ \text{Å} \leqslant \Delta r \leqslant 0.375\ \text{Å}$, $-0.175\ \text{Å} \leqslant \Delta R \leqslant 0.25\ \text{Å}$ and $0^\circ \leqslant \theta \leqslant 60^\circ$. Here, Δr and ΔR are the CH and CS bond stretching coordinates, respectively, and the angle θ measures the deviation from linearity. The chosen coordinate ranges provide an accurate representation of the potential energy of HCS^+ up to about $10{,}000\ \mathrm{cm}^{-1}$. Individual contributions to the composite PEF (denoted by index α) are represented in polynomial form according to:

$$V^\alpha - V^\alpha_{\mathrm{ref}} = \sum_{ijk} C^\alpha_{ijk} \Delta r^i \Delta R^j \theta^k \qquad (\mathrm{k:\ even}) \tag{1}$$

The coefficients C^α_{ijk} are determined through least-square fits and are supplied as Supplementary Information (Table S1 and S2). A composite PEF is then obtained by summation of the individual contributions and transformation of the resulting polynomial to its minimum. Due to the inclusion of the DBOC contribution the final composite PEFs differ between the HCS^+ isotopologues. The PEFs are provided in Table S3 of the Supplementary Material for the four most important species ($H^{12}C^{32}S^+$, $D^{12}C^{32}S^+$, $H^{13}C^{32}S^+$ and $H^{32}C^{34}S^+$).

In addition to the PEF necessary to obtain the rovibrational wavefunctions, an electric dipole moment function (EDMF) is developed in order to allow for the calculation of transition dipole moments and band intensities. The F12b/VQZ-F12 method is employed in finite field calculations with field strengths of ±0.0003 a.u. in the relevant Cartesian directions. Dipole moments are evaluated in the same coordinate ranges as for the PEF. Local transformation of the electric dipole moment vector to the Eckart system of coordinates yields the parallel $\mu^\parallel$ and perpendicular $\mu^\perp$