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REGULAR ARTICLE

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Theoretical study of the C_3S molecule

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Abstract For the most stable linear isomer of C_3S in its $X^1\Sigma^+$ state a six-dimensional potential energy surface (PES) has been calculated ab initio by coupled cluster – connected triples (CCSD(T)) method. The analytic form of the PES has been transformed in a quartic force field in dimensionless normal coordinates and employed in calculations of spectroscopic constants using second-order perturbation theory. The PES and the full kinetic energy operator in internal coordinates have been used to calculate variationally the anharmonic ro-vibrational energies for $J = 0$ and $J = 1$. The two experimental band origins of C_3S observed in the gas phase, ν_1 and $\nu_1+\nu_5-\nu_5$, agree very well with the theoretical values. The anharmonic ro-vibrational levels, including the bending modes up to 2200 cm^{-1}, are reported. The singlet ground state PES has a saddle point at about 1.25 eV above the linear minimum and two other higher lying cyclic local minima. The only dipole- and spin-allowed electronic transition between 0 and 5 eV is calculated to be the $^1\Pi - X^1\Sigma^+$ transition with a vertical transition energy of 353.2 nm in good agreement with the matrix value of 378 nm. The dissociative paths C + C_2S, C_2 + CS and C_3 + S of low lying singlet and triplet states have been investigated.

Dedicated to Professor H. Stoll.

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1 Introduction

The 3-thioxo-1,2-propadienylidene, C_3S, has been identified in outer space by its rotational transitions and is one of the abundant sulphur-containing molecules involved in the chemistry within dense interstellar clouds [1–4]. For the most stable linear isomer of C_3S in its $^1\Sigma^+$ electronic ground state rotational spectra for four isotopomers were used to determine its substitution structure (r_s) [5–7]. In the excited bending vibrational states of the v_4 and v_5 modes rotational transitions have been analysed in terms of vibration–rotation interaction terms. So far, the only experimental vibrational band origins observed in the gas phase IR spectrum are ν_1 and the hot band $\nu_1 + \nu_5 - \nu_5$ [8]. In the Ar-matrix the transitions to all three stretch fundamentals, one overtone and three stretch combination states, corresponding to the most intense IR transitions of C_3S have been observed [9]. In the same experiment the UV spectrum scanned between 220 and 600 nm revealed only one electronic transition at 378 nm tentatively attributed to C_3S [9]. The neutralisation-ionization mass-spectrometric study showed that the linear isomer does not easily undergo rearrangements, during the timeframe of this experiment [10].

The most extensive theoretical study of the electronic ground state of C_3S has been published by Botschwina and Seeger et al. [11, 14]. In these works the most accurate results were obtained by the coupled cluster method including the quasi-perturbative treatment of the connected triple substitutions (CCSD(T)). Multidimensional potential energy and dipole moment surfaces were used in calculations of spectroscopic constants, anharmonic wavenumbers for the transitions from the vibrational ground state to the 20 lowest excited stretching vibrational states including their absolute absorption intensities. The theoretical data were combined with experiments to deduce the B_e rotational constant and the r_e structure. The approximate variational procedure employed in the calculations of the excited stretching states yielded valuable results for the assignment of the IR matrix spectrum. Differences in the calculated and experimental band origins did not exceed 26 cm^{-1}. The ground state

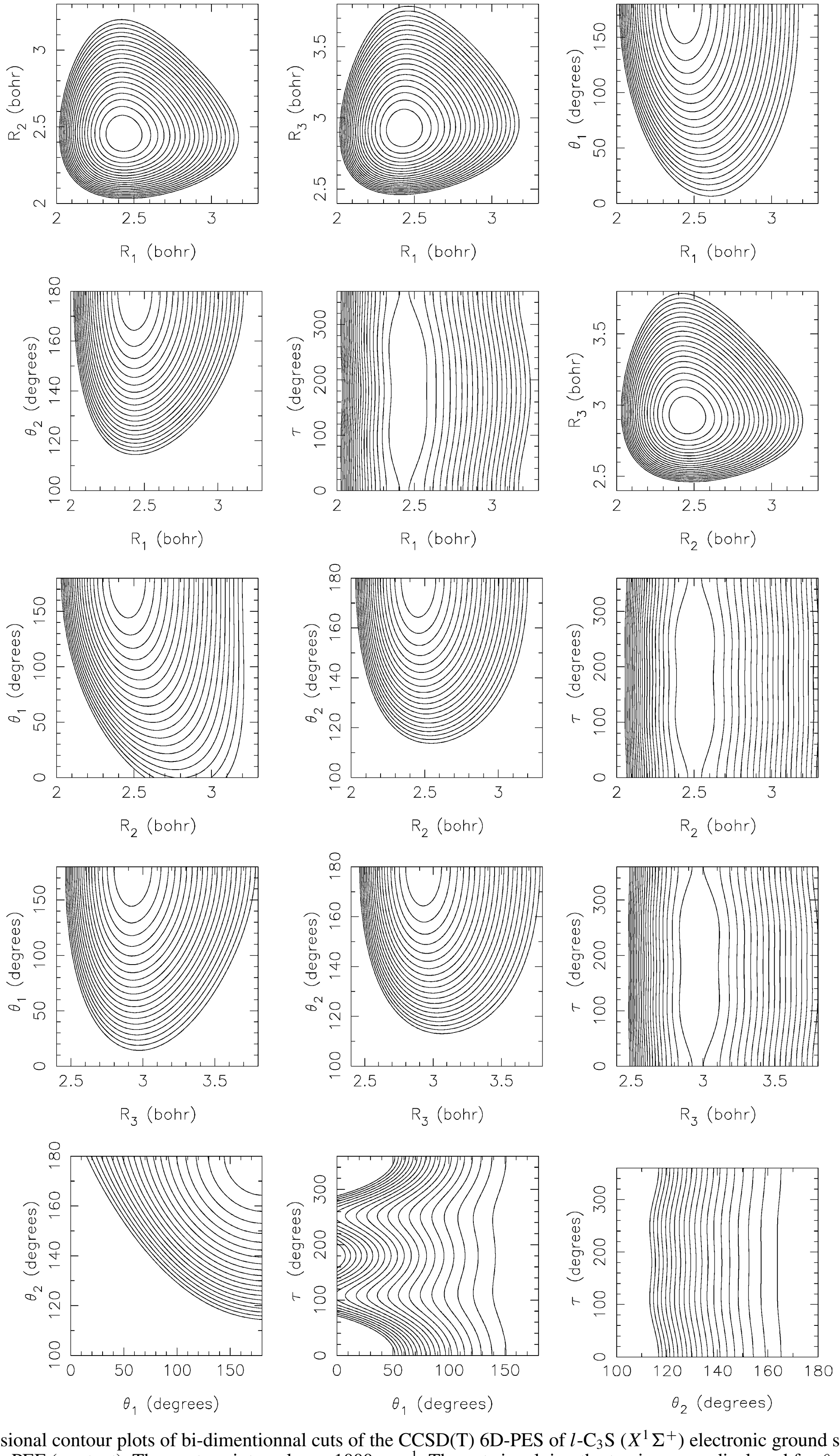


Fig. 1 Two dimensional contour plots of bi-dimentionnal cuts of the CCSD(T) 6D-PES of l-C$_3$S ($X^1\Sigma^+$) electronic ground state for all permutations defining the PEF (see text). The contour intervals are $1000\,\mathrm{cm}^{-1}$. The cuts involving the torsion τ are displayed for θ_1 and/or θ_2 equal to 140°

Table 1 Harmonic (ω) and anharmonic wavenumbers (ν) and anharmonic constants (x_{ij}) of l-C_3S ($X^1\Sigma^+$). All values are in cm^{-1}

ω_1	2086.0^a	ω_2	1532.7^a	ω_3	723.8^a	ω_4	481.2^a	ω_5	147.1^a
	2099.7^b		1536.1^b		723.3^b		487^b		155.2^b
ν_1	2046.9^a	ν_2	1515.7^a	ν_3	715.7^a	ν_4	474.7^a	ν_5	144.4^a
	2071.0^b		1520.1^b						
	2057.0^c		1520.3^c		717.4^c		475.8^c		145.0^c
	2058.2^d								
	2046.2^e		1533.7^e		725.6^e				
$G(0)$	2758.2^a	$\nu_{1+}\nu_{5-}\nu_5$	2054.3^c						
	2768.1^c		2053.0^d						
x_{11}	−8.8	x_{33}	−1.2	x_{22}	−3.7	x_{55}	−0.6	x_{12}	−14.3
x_{34}	−7.5	x_{23}	−2.0	x_{l4l4}	−1.8	x_{13}	−6.5	x_{35}	6.1
x_{24}	−2.5	x_{1415}	0.7	x_{14}	−6.1	x_{44}	2.0	x_{25}	1.0
x_{1515}	0.9	x_{15}	−5.0	x_{45}	−2.8				
			−5.18^d						

[a] This work. Perturbative treatment
[b] Ref. [14]
[c] This work. Variational treatment
[d] Ref. [8]
[e] Ref. [9]

electric dipole moment was determined to be μ_o = 3.704(9) debye, whereas the theoretical CCSD(T) μ_e value was calculated to be 3.89 debye [12–14]. Other theoretical works dealt with harmonic vibrations, equilibrium distances, the possible mechanism of the C_3S formation, and rearrangements [10, 13–16].

In the present work a new 6D PES for the linear C_3S ground state has been generated and employed in the calculations of the spectroscopic constants and anharmonic ro-vibrational energies, including also the ν_4 and ν_5 bendings, their overtones and combination states, which have not yet been known. The vertical electronic excitation energies helped to assign the C_3S UV matrix spectrum. Apart from its global linear minimum, C_3S possesses in its ground state PES a low-lying saddle point and local minima for cyclic isomers, for which the equilibrium geometries and harmonic wavenumbers have been calculated. In the context of possible rearrangements of linear C_3S, the dissociation paths of the ground and excited states to several asymptotes have been investigated.

2 Electronic structure calculations

The electronic calculations have been performed using MOLPRO [17]. For carbon and sulphur atoms the *spdf* subset of the cc-pVQZ basis set of Dunning [18] was used. The dissociation pathways have been investigated at the complete active space self consistent field (CASSCF) [19,20] level of theory. The nine lowest σ and the first π molecular orbitals were kept doubly occupied and the electronic states with the same spin multiplicity were averaged together with equal weights. The PES of the l-C_3S $X^1\Sigma^+$ state and the stationary points on the ground state PES were calculated by the coupled cluster method including the perturbative treatment of the connected triple substitutions (CCSD(T)), and all valence electrons were correlated [21].

3 Potential energy surface of the linear C_3S electronic ground state

The 6D-PES of l-C_3S ($X^1\Sigma^+$) is mapped in internal coordinates comprising the three stretching coordinates R_1 (external CC bound), R_2 (central CC), and R_3 (CS stretch), the two in-plane bending angles θ_1 (CCC) and θ_2 (CCS), and the torsional angle τ between the CCC and CCS planes. This PEF is calculated around the reference structure: R_1 = 1.270 Å, R_2 = 1.296 Å, and R_3 = 1.540 Å for 210 different geometries. The energies were fitted to the analytical form

$$V(R_1, R_2, R_3, \theta_1, \theta_2, \tau) = \sum_{ijklmn} C_{ijklmn} Q_1^i Q_2^j Q_3^k Q_4^l Q_5^m Q_6^n$$

where $Q_u = \frac{R_i - R_i^{\text{ref}}}{R_i}$ for $u = 1, 2, 3$ and $0 \leq R_i$.

For the bending; $Q_u = \theta_{u-3} - \theta_{u-3}^{\text{ref}}$ for $u = 4, 5$ and $0° \leq \theta_u \leq 180°$

and $Q_6^n = \cos(n\tau)$ for $0° \leq \tau \leq 360°$.

The index 'ref' indicates the reference geometry used for the fit.

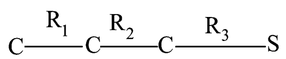
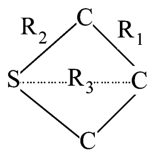
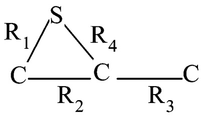
The geometries were chosen in the range: $2.0 \leq R_1 \leq 2.8$, $2.05 \leq R_2 \leq 2.85$, $2.6 \leq R_3 \leq 3.4$ (in bohr), $120° \leq \theta_1 \leq 180°$, $120° \leq \theta_2 \leq 180°$, and $0° \leq \tau \leq 180°$. In the polynomial expansion, the exponents were restricted to $i + j + k + l + m + n \leq 4$ and $n \leq 2$, leading to 147 C_{ijklmn} coefficients. The root mean square error of the fit was less than 3 cm^{-1}. The expansion is valid for energies up to about 9000 cm^{-1} above the minimum. The PES was used to obtain the full quartic force fields in internal and dimensionless normal coordinates. The latter expansion allowed to calculate the spectroscopic constants by second-order perturbation from the expressions of Refs. [22,23]. The PES's can be obtained on request.

Figure 1 depicts the 15 two-dimensional cuts of the CCSD(T) PES for all permutations of the internal coordinates (the other internal coordinates were kept fixed at their equilibrium values in l-C_3S($X^1\Sigma^+$)), except those involving τ, which are displayed for θ_1 = 140°. The step between the

Table 2 Variationally calculated ro-vibrational spectrum of *l*-C_3S ($X^1\Sigma^+$)

J=0				J=1	
σ^+		σ^-		π	
$(V_1 V_2 V_3 V_4^{l_4} V_5^{l_5})$	E/cm $^{-1}$	$(V_1 V_2 V_3 V_4^{l_4} V_5^{l_5})$	E/cm $^{-1}$	$(V_1 V_2 V_3 V_4^{l_4} V_5^{l_5})$	E/cm $^{-1}$
$(0\ 0\ 0\ 0^0\ 0^0)$	0.0	$(0\ 0\ 0\ 1^1\ 1^1)$	620.7	$(0\ 0\ 0\ 0^0\ 1^1)$	145.0
$(0\ 0\ 0\ 0^0\ 2^0)$	289.2	$(0\ 0\ 0\ 1^1\ 3^1)$	904.2	$(0\ 0\ 0\ 0^0\ 3^1)$	433.6
$(0\ 0\ 0\ 0^0\ 4^0)$	574.0	$(0\ 0\ 0\ 1^1\ 5^1)$	1183.9	$(0\ 0\ 0\ 1^1\ 0^0)$	475.8
$(0\ 0\ 0\ 1^1\ 1^1)$	620.9	$(0\ 0\ 0\ 2^2\ 2^2)$	1239.2	$(0\ 0\ 0\ 0^0\ 5^1)$	724.9
$(0\ 0\ 1\ 0^0\ 0^0)$	717.4	$(0\ 0\ 1\ 1^1\ 1^1)$	1335.0	$(0\ 0\ 0\ 1^1\ 2^0)$	764.5
$(0\ 0\ 0\ 0^0\ 6^0)$	857.2	$(0\ 0\ 0\ 1^1\ 7^1)$	1462.0	$(0\ 0\ 0\ 1^1\ 2^2)$	771.1
$(0\ 0\ 0\ 1^1\ 3^1)$	907.6	$(0\ 0\ 0\ 2^2\ 4^2)$	1522.8	$(0\ 0\ 1\ 0^0\ 1^1)$	866.9
$(0\ 0\ 0\ 2^0\ 0^0)$	961.9	$(0\ 0\ 0\ 3^1\ 1^1)$	1587.7	$(0\ 0\ 0\ 0^0\ 7^1)$	1044.1
$(0\ 0\ 1\ 0^0\ 2^0)$	1015.5	$(0\ 0\ 1\ 1^1\ 3^1)$	1627.4	$(0\ 0\ 0\ 1^1\ 4^0)$	1070.3
$(0\ 0\ 0\ 0^0\ 8^0)$	1145.5	$(0\ 0\ 0\ 1^1\ 9^1)$	1743.1	$(0\ 0\ 0\ 1^1\ 4^2)$	1084.1
$(0\ 0\ 0\ 1^1\ 5^1)$	1197.5	$(0\ 0\ 0\ 2^2\ 6^2)$	1808.8	$(0\ 0\ 0\ 2^2\ 1^1)$	1099.3
$(0\ 0\ 0\ 2^2\ 2^2)$	1239.5	$(0\ 0\ 0\ 3^3\ 3^3)$	1856.6	$(0\ 0\ 0\ 2^0\ 1^1)$	1107.8
$(0\ 0\ 0\ 2^0\ 2^0)$	1247.5	$(0\ 0\ 0\ 3^1\ 3^1)$	1870.9	$(0\ 0\ 1\ 0^0\ 3^1)$	1165.6
$(0\ 0\ 1\ 0^0\ 4^0)$	1309.5	$(0\ 0\ 1\ 1^1\ 5^1)$	1916.9	$(0\ 0\ 1\ 1^1\ 0^0)$	1186.2
$(0\ 0\ 1\ 1^1\ 1^1)$	1336.8	$(0\ 0\ 1\ 2^2\ 2^2)$	1954.4	$(0\ 0\ 0\ 0^0\ 9^1)$	1391.0
$(0\ 0\ 2\ 0^0\ 0^0)$	1441. 7	$(0\ 0\ 2\ 1^1\ 1^1)$	2033.6	$(0\ 0\ 0\ 1^1\ 6^0)$	1405.5
$(0\ 0\ 0\ 0^0\ 10^0)$	1449.6	$(0\ 0\ 0\ 1^1\ 11^1)$	2054.6	$(0\ 0\ 0\ 1^1\ 6^2)$	1424.6
$(0\ 0\ 0\ 1^1\ 7^1)$	1497.7	$(0\ 0\ 0\ 2^2\ 8^2)$	2098.5	$(0\ 0\ 0\ 3^1\ 0^0)$	1428.9
$(0\ 0\ 0\ 2^2\ 4^2)$	1519.6	$(0\ 1\ 0\ 1^1\ 1^1)$	2133.6	$(0\ 0\ 0\ 2^2\ 3^1)$	1448.0
$(0\ 1\ 0\ 0^0\ 0^0)$	1520.3	$(0\ 0\ 0\ 3^3\ 5^3)$	2139.1	$(0\ 0\ 0\ 2^2\ 3^3)$	1449.4
$(0\ 0\ 0\ 2^0\ 4^0)$	1543.7	$(0\ 0\ 0\ 3^1\ 5^1)$	2162.6	$(0\ 0\ 0\ 2^0\ 3^1)$	1461.7
$(0\ 0\ 1\ 0^0\ 6^0)$	1590.6	$(0\ 0\ 0\ 4^2\ 2^2)$	2205.8	$(0\ 0\ 1\ 0^0\ 5^1)$	1474.7
$(0\ 0\ 0\ 3^1\ 1^1)$	1603.6			$(0\ 0\ 1\ 1^1\ 2^0)$	1489.4
$(0\ 0\ 1\ 1^1\ 3^1)$	1635.5			$(0\ 0\ 1\ 1^1\ 2^2)$	1498.1
$(0\ 0\ 1\ 2^0\ 0^0)$	1668.1			$(0\ 0\ 2\ 0^0\ 1^1)$	1595.1
$(0\ 0\ 2\ 0^0\ 2^0)$	1747.3			$(0\ 1\ 0\ 0^0\ 1^1)$	1665.8
$(0\ 0\ 0\ 0^0\ 12^0)$	1771.9			$(0\ 0\ 0\ 0^0\ 11^1)$	1700.6
$(0\ 0\ 0\ 1^1\ 9^1)$	1796.0			$(0\ 0\ 0\ 2^2\ 5^1)$	1726.9
$(0\ 1\ 0\ 0^0\ 2^0)$	1811.4			$(0\ 0\ 0\ 2^2\ 5^3)$	1760.8
$(0\ 0\ 0\ 2^2\ 6^2)$	1820.7			$(0\ 0\ 0\ 2^0\ 5^1)$	1762.1
$(0\ 0\ 0\ 2^0\ 6^0)$	1857.5			$(0\ 0\ 1\ 1^1\ 4^0)$	1776.9
$(0\ 0\ 0\ 3^3\ 3^3)$	1861.4			$(0\ 0\ 1\ 2^2\ 1^1)$	1795.9
$(0\ 0\ 0\ 3^1\ 3^1)$	1890.6			$(0\ 0\ 1\ 2^0\ 1^1)$	1812.7
$(0\ 0\ 1\ 0^0\ 8^0)$	1905.4			$(0\ 0\ 0\ 3^3\ 2^2)$	1814.1
$(0\ 0\ 0\ 4^0\ 0^0)$	1941.3			$(0\ 0\ 1\ 0^0\ 7^1)$	1825.2
$(0\ 0\ 1\ 1^1\ 5^1)$	1943.2			$(0\ 0\ 0\ 3^1\ 2^0)$	1837.2
$(0\ 0\ 1\ 2^2\ 2^2)$	1953.3			$(0\ 0\ 0\ 3^1\ 2^2)$	1849.6
$(0\ 0\ 1\ 2^0\ 2^0)$	1970.7			$(0\ 0\ 2\ 1^1\ 0^0)$	1903.2
$(0\ 0\ 2\ 0^0\ 4^0)$	2050.1			$(0\ 0\ 0\ 0^0\ 13^1)$	1904.3
$(1\ 0\ 0\ 0^0\ 0^0)$	2057.0			$(0\ 0\ 0\ 1^1\ 8^0)$	1913.8
$(0\ 0\ 2\ 1^1\ 1^1)$	2059.7			$(0\ 0\ 0\ 1^1\ 8^2)$	1956.7
$(0\ 0\ 0\ 1^1\ 11^1)$	2075.0			$(0\ 0\ 2\ 0^0\ 3^1)$	1960.2
$(0\ 1\ 0\ 0^0\ 4^0)$	2098.1			$(0\ 0\ 0\ 1^1\ 10^0)$	1992.7
$(0\ 0\ 0\ 2^2\ 8^2)$	2129.1			$(0\ 0\ 0\ 1^1\ 10^2)$	2022.6
$(0\ 1\ 0\ 1^1\ 1^1)$	2139.6			$(0\ 1\ 0\ 0^0\ 3^1)$	2058.8
$(0\ 0\ 0\ 2^0\ 8^0)$	2141.1			$(0\ 0\ 0\ 2^2\ 7^1)$	2079.9
$(0\ 0\ 3\ 0^0\ 0^0)$	2162.5			$(0\ 0\ 0\ 2^2\ 7^3)$	2087.2
$(0\ 0\ 0\ 3^3\ 5^3)$	2197.0			$(0\ 0\ 0\ 2^0\ 7^1)$	2092.0
$(0\ 0\ 0\ 3^1\ 5^1)$	2200.8			$(0\ 0\ 1\ 0^0\ 9^1)$	2113.6
				$(0\ 0\ 0\ 4^2\ 1^1)$	2124.5
				$(0\ 0\ 0\ 4^0\ 1^1)$	2135.2
				$(0\ 0\ 1\ 1^1\ 6^2)$	2144.5
				$(0\ 0\ 1\ 1^1\ 6^0)$	2163.0
				$(0\ 0\ 1\ 2^2\ 3^1)$	2180.5
				$(0\ 0\ 1\ 2^2\ 3^3)$	2186.6
				$(0\ 0\ 1\ 2^0\ 3^1)$	2194.2
				$(1\ 0\ 0\ 0^0\ 1^1)$	2199.3

Table 3 *spdf* cc-pVQZ CCSD(T) and *spd* cc-pVTZ CCSD(T) computations on the isomers of C$_3$S, their relative energies (in eV) and their harmonic wavenumbers (in cm^{-1}). All distances are in bohr

C$_3$S isomer		R$_1$	R$_2$	R$_3$	R$_4$	Relative Energy	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
	*l*-C$_3$S (X$^1\Sigma^+$)	2.432	2.452	2.928		0^a	2086.0 (σ^+)	1532.7 (σ^+)	723.8 (σ^+)	481.2 (π)	147.1 (π)	
	*r*-C$_3$S (X^{1}A$_1$)	2.687 2.684^b 2.697^c	3.327 3.330^b 3.350^c	5.291 5.321^b 5.315^c		2.40 2.24^b	1374.7 (a$_1$)^c	915.4 (a$_1$)^c	664.6 (a$_1$)^c	415.4 (b$_1$)^c	746.6 (b$_2$)^c	158.8 (b$_2$)^c
	*c*-CSC$_2$ (X^{1}A')	3.278 3.291^b 3.263^c	2.746 2.705^b 2.719^c	2.472 2.474^b 2.471^c	3.429 3.436^b 3.512^c	2.96 2.76^b	1684.2 (a')^c	958.1 (a')^c	638.0 (a')^c	581.5 (a')^c	146.7 (a')^c	278.2 (a")^c

[a] Used as reference. Total CCSD(T) energy at the equilibrium geometry of *l*-C$_3$S(X$^1\Sigma^+$) is -511.63882032 a.u.
[b] Ref. [10]
[c] Calculated at the *spd* cc-pVTZ CCSD(T) level of theory
[d] Saddle point

contours is 1000 cm^{-1}. The R_1 and R_2 (CC stretches) are weakly coupled, also with the in-plane bendings (θ_1 and θ_2). The cuts involving the torsion angle τ show that this coordinate is coupled with all other internal coordinates and that the shapes change strongly for $\tau \sim 100°$ (similar PES shapes in C$_3$O or NCCN [24,25]). The cubic expansion in five coordinates of Botschwina et al. [14], in which the torsion has been neglected, is in a good agreement for the bending and stretch-bending parts of the present PES, as follows from the comparison of the harmonic wavenumbers in the following section.

4 Spectroscopic data for the X$^1\Sigma^+$ state and the C$_3$S isomers

The spectroscopic constants calculated from the CCSD(T) quartic force field in dimensionless normal coordinates agree well with the theoretical results of Ref. [11]. Our r_e distances obtained from the fit of the calculated points are longer by about 0.005 – 0.009 Å than the values of Ref. [11] calculated by combining the experimental rotational constants for four different isotopomers with the CCSD(T) $B_e - B_o$ differences. The sets of α constants and the ro-vibrational constants q_i are in good agreement with experimental and theoretical values of Refs. [11] and [14]. In Table 1 we give harmonic and anharmonic wavenumbers and the full set of anharmonic constants x$_{ij}$. The present harmonic wavenumbers agree to within better than 8 cm^{-1}, apart from ω_1, with those of Ref. [14].

Table 4 Electronic configuration and vertical excitation energies (in eV) of the lowest excited states of *l*-C$_3$S

Electronic state	T_e	Dominant electronic configuration
$X^1\Sigma^+$	0.0^a	$\sigma^2\sigma^2\pi^4\pi^4$
$a^3\Pi$	2.50	$\sigma^2\sigma^1\pi^4\pi^4\pi^1$
$B^3\Sigma^+$	2.78	$\sigma^2\sigma^2\pi^4\pi^3\pi^1$
$C^3\Delta$	3.01	$\sigma^2\sigma^2\pi^4\pi^3\pi^1$
$D^3\Sigma^-$	3.18	$\sigma^2\sigma^2\pi^4\pi^3\pi^1$
$A^1\Sigma^-$	3.18	$\sigma^2\sigma^2\pi^4\pi^3\pi^1$
$B^1\Delta$	3.20	$\sigma^2\sigma^2\pi^4\pi^3\pi^1$
$C^1\Pi$	3.51	$\sigma^2\sigma^1\pi^4\pi^4\pi^1$
$C^3\Pi$	5.74	$\sigma^2\sigma^1\pi^4\pi^3\pi^2$
$D^1\Pi$	6.96	$\sigma^2\sigma^1\pi^4\pi^3\pi^2$

[a] Total CASSCF energy at the equilibrium geometry of *l*-C$_3$S(X$^1\Sigma^+$) (see Table 1) is -511.201074 a.u

The 6D-PES was used in variational calculations of the nuclear motion problem with the full Hamiltonian in internal coordinates [26]. A contraction scheme was applied in order to improve the convergence and reduce the size of the matrices. First, two-dimensional contractions were performed with primitive Hermite polynomials basis for R_1 and R_3 stretches. The resulting functions were then combined with the similarly precontracted stretching functions associated with R_2. The three-dimensional stretching functions were contracted and stored. Then, four different contractions were performed for the bendings: two by combining the θ_1 and θ_2 basis functions with $\cos(0\tau)$ and $\cos(1\tau)$; and

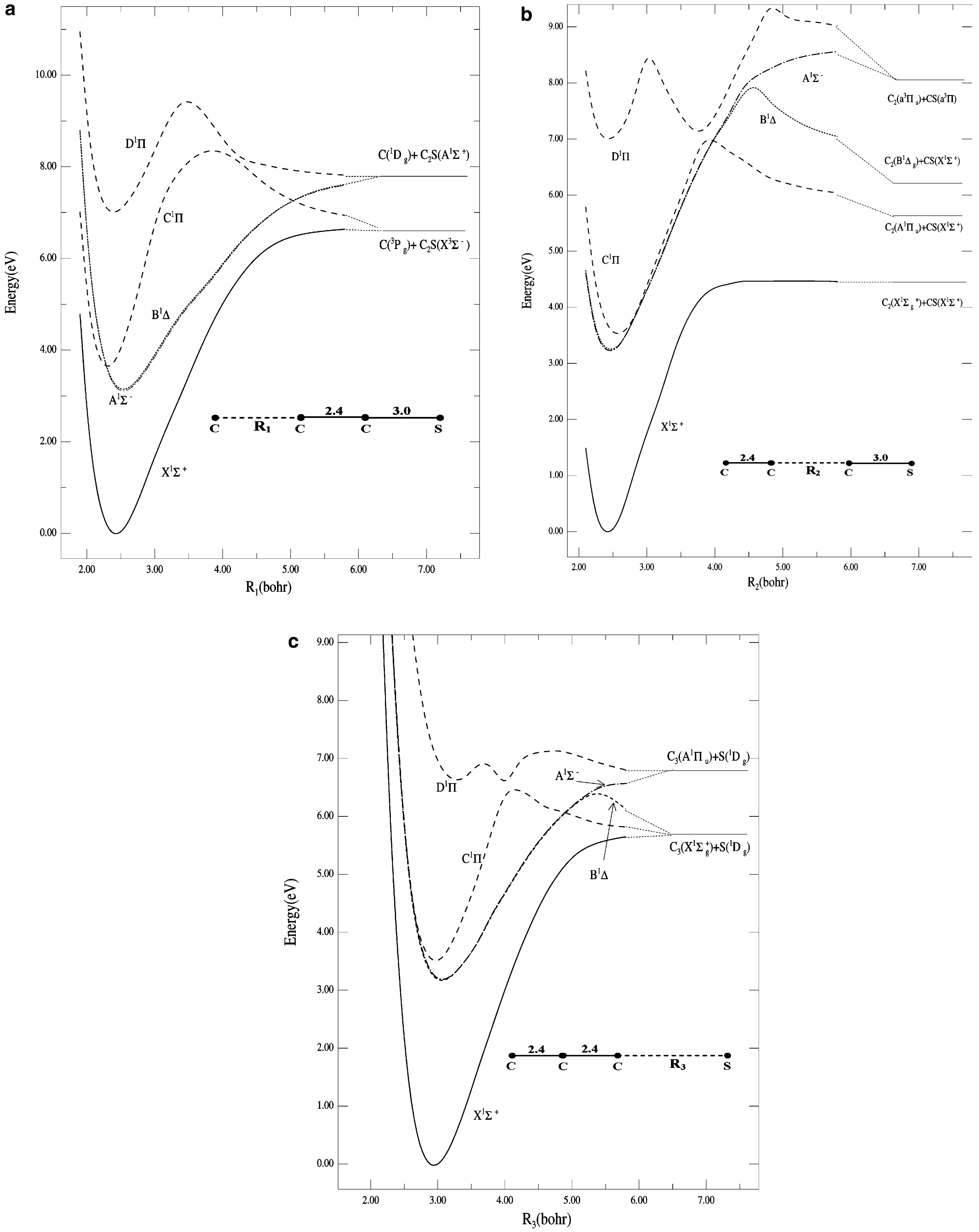


Fig. 2 CASSCF collinear one-dimensional cuts of the PESs of the lowest singlet electronic states of *l*-C_3S along the stretching coordinates. In **A** the other distances are set to $R_2 = 2.4$ bohr and $R_3 = 3.0$ bohr. In **B** the other distances are set to $R_1 = 2.4$ bohr and $R_3 = 3.0$ bohr. In **C** R_1 and R_2 are set to 2.4 bohr

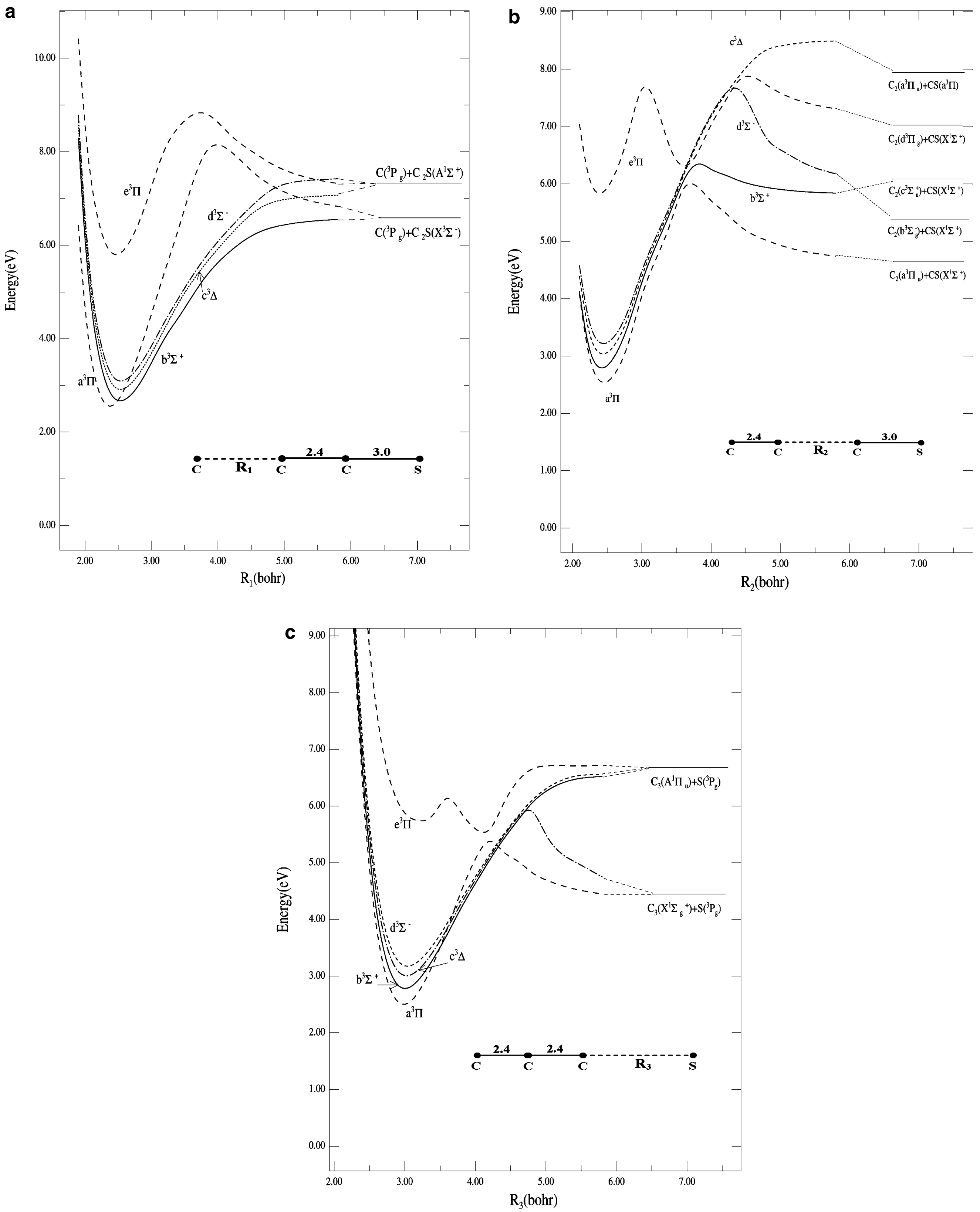


Fig. 3 CASSCF collinear one-dimensional cuts of the PESs of the lowest triplet electronic states of *l*-C_3S along the stretching coordinates. In **A** the other distances are set to $R_2 = 2.4$ bohr and $R_3 = 3.0$ bohr. In **B** the other distances are set to $R_1 = 2.4$ bohr and $R_3 = 3.0$ bohr. In **C** R_1 and R_2 are set to 2.4 bohr

two with $\sin(1\tau)$ and $\sin(2\tau)$. The resulting functions were combined to M primitive τ functions: $\cos(0\tau)$ to $\cos(M\tau)$ and $\sin(1\tau)$ to $\sin(M\tau)$. The ro-vibrational levels were obtained by diagonalization of the full Hamiltonian matrix with the precontracted vibrational basis and eigenfunctions of the rigid rotor. In the present work, calculations were done for $J = 0$ and 1.

Our perturbational and variational (Table 1) anharmonic wavenumbers for the fundamentals agree to within about $1\,\mathrm{cm}^{-1}$ for the bending modes and to within about $10\,\mathrm{cm}^{-1}$ for the stretching modes. The two gas phase experimental band origins ν_1 and $\nu_1 + \nu_5 - \nu_5$ are in excellent agreement with our variational results, though this is somewhat fortuitous considering the theoretical ansatz used. In Table 2 we give ro-vibrational levels for $J = 0$ and $J = 1$ calculated by this approach up to $2200\,\mathrm{cm}^{-1}$. The ν_2 and ν_3 stretches are in very good agreement with the values of Ref. [14], the experimental matrix values differ by $13\,\mathrm{cm}^{-1}$ and $7\,\mathrm{cm}^{-1}$. Apart from the hot band including ν_5 neither experimental nor theoretical anharmonic wavenumbers for the bending levels have been known. For higher lying states, the assignment with harmonic quantum numbers is only tentative due to anharmonic mixings between interacting states. The IR matrix spectrum and the theoretical calculations of Botschwina [11] showed that the large intensities of the stretching vibrations, their overtones and combination levels allow their detection even in the regions with very high density of ro-vibrational states.

In Table 3 the geometries, relative energies, and harmonic wavenumbers for two additional local minima and one saddle point on the ground state PES are presented. The geometries are compared with previous DFT results of Tran et al. [10]. The three-membered ring and the four-membered ring isomers are calculated to lie about 2.94 and 2.4 eV above the global linear minimum. The saddle point with the three-membered carbon ring lies much lower and could possibly open the path for a degenerate rearrangement ^{13} C^{12} C^{12} C^{32} S $\leftrightarrow {}^{12}$C^{12}C^{13}C^{32}S. However, considering the high density of vibrational states at the energy of the saddle point it is difficult to locate a mode-specific path for this intramolecular process. Depending on the precursors, the C_3S molecule might be formed in other forms than the most stable one. The calculated differences in the structures and vibrational wavenumbers can be helpful for their identification.

5 Electronically excited states and dissociation paths of C_3S

In Table 4 we give the vertical transition energies calculated by CASSCF approach for the CCSD(T) equilibrium geometry of C_3S $X^1\Sigma^+$ (Sect. 3) and the dominant configurations of each electronic state. Only one dipole- and spin-allowed electronic transition is calculated in the energy range between 0 and 5 eV, in accordance with the UV matrix spectrum, in which only one electronic transition has been detected which, however, remained unassigned. The $\mathrm{C}^1\Pi - X^1\Sigma^+$ transition is calculated at 3.51 eV in good agreement with the matrix value of 3.32 eV [9]. The calculated vertical excitation energies suggest that different type of interactions, for instance, spin-orbit, vibronic, or Renner-Teller couplings will complicate the interpretation of UV absorption or emission spectra. Moreover, the present approach is not suited to calculate Rydberg states, which could require more diffuse basis functions and larger active space.

In Fig. 2 we show the collinear dissociation paths along the stretching coordinates for the ground and electronically excited states for the singlets and in Fig. 3 for the triplets. The energetically lowest dissociation path of the ground state of singlet multiplicity leads to C_2 + CS, followed by C_3 + S and C + C_2S. No avoided crossings or barriers on these paths have been calculated. The $a^3\Pi$ state has a barrier on the collinear dissociation path due to the avoided crossing with the $e^3\Pi$ state. The lowest dissociation asymptote in this case is C_3 + S. Both figures show that the $\mathrm{C}^1\Pi$ state is embedded in the region of several triplet states. The cuts along the *cis*-bending coordinate [27] show that the $\mathrm{C}^1\Pi$ state forms a bent/linear Renner-Teller pair, whereas all other doubly degenerate states lead to linear/linear pairs. Similarly, the *trans*-bending cuts show that in none of the Π or Δ states bent minima on the A$'$ or A$''$ sheets of the PES exist [27].

6 Conclusions

For the tetra-atomic linear molecule C_3S the ro-vibrational anharmonic wavenumbers for $J = 0$ and 1 up to $2200\,\mathrm{cm}^{-1}$ has been calculated by using variational approach and 6D-PES. The results are in good agreement with existing experiments and previous theoretical data. The calculated anharmonic bending modes, their overtones, and combination states have not yet been known. The only UV transition detected in the matrix has been assigned to belong to the $\mathrm{C}^1\Pi - X^1\Sigma^+$ transition.

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