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Cite this: DOI: 10.1039/xxxxxxxxxx

Inelastic Vibrational Dynamics of CS in Collision with H₂ Using a Full-dimensional Potential Energy Surface[†]

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Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

We report a six-dimensional (6D) potential energy surface (PES) for the CS-H₂ system computed using high-level electronic structure theory and fitted using a hybrid invariant polynomial method. Full-dimensional quantum close-coupling scattering calculations have been carried out using this potential for rotational and, for the first time, vibrational quenching transitions of CS induced by H₂. State-to-state cross sections and rate coefficients for rotational transitions in CS from rotational levels $j_1=0-5$ in the ground vibrational state are compared with previous theoretical results obtained using a rigid-rotor approximation. For vibrational quenching, state-to-state and total cross sections and rate coefficients were calculated for the vibrational transitions in CS($v_1 = 1, j_1$)+H₂($v_2 = 0, j_2$) → CS($v'_1 = 0, j'_1$)+H₂($v'_2 = 0, j'_2$) collisions, for $j_1=0-5$. Cross sections for collision energies in the range 1 to 3000 cm⁻¹ and rate coefficients in the temperature range of 5 to 600 K are obtained for both para-H₂ ($j_2=0$) and ortho-H₂ ($j_2=1$) collision partners. Application of the computed results in astrophysics is also discussed.

1 Introduction

Quantum mechanical calculations of molecular scattering are of great interest for chemical dynamics and astrophysics studies¹. Carbon monosulfide (CS), the sulfur analogue of carbon monoxide, was first detected by Penzias et al.² through the line emission of $J = 3 - 2$ in four sources including Orion A, W51, IRC+10216, and DR 21. It is also the first sulfur-containing molecule observed in interstellar space. Since then numerous observations of CS have been reported³⁻¹⁰ in a variety interstellar regions. Observations of the CS emission lines are very useful for investigation of the molecular gas and its composition. An accurate prediction of the abundance of CS in the interstellar medium requires its collisional rate coefficients with ambient species. So far available collisional rate coefficients are limited to rigid-rotor calculations for a small range of rotational transitions in the vibrational ground state¹¹⁻¹⁴. In interstellar clouds, molecular hydrogen is the most abundant species and the dominant collision partner. Therefore, the vibrational and rotational rate coefficients of CS by H₂ impact is of great importance in astrophysics, astrochemistry, and in

interstellar regions where non-equilibrium process plays a dominant role. In particular, with the detection of CS in vibrationally excited states, the rovibrational rate coefficients are needed to analyze CS lines and model the emission and thermal balance in the interstellar medium.

Due to its astrophysical importance, there have been many theoretical studies of pure rotational cross sections and rate coefficients for CS in collision with H₂. Green and Chapman¹¹ calculated CS-H₂ rotational excitation rate coefficients among first 13 rotational states of CS. Later Turner et al.¹² extended the calculations to rotational levels through $j_1 = 20$ for rate coefficient below 300 K. However these rate coefficients were computed using a CS-He PES obtained from an electron gas model¹⁵. Vastel et al.¹⁰ performed local thermodynamic equilibrium (LTE) and non-LTE radiative transfer modeling using the NAUTILUS chemical code for the sulfur chemistry in the L1544 pre-stellar core; the rate coefficients of CS with para-H₂ calculated by Green and Chapman¹¹ were adopted to obtain the column density of CS. Albrecht presented approximate rate coefficients for CS-H₂ ($j_2 = 0$) using an empirical analytical expression¹⁶ and a fit to the rate coefficients of Green and Chapman¹¹. This approximation was also adopted to derive the collisional rate coefficients of linear molecules SiO, HCN, H₂O^{17,18}. Recently, a four-dimensional (4D) potential energy surface (PES) for CS-H₂ was constructed by Denis-Alpizar et al.²⁰ based on ab initio calculations within the coupled-cluster singles and doubles plus perturbative triples [CCSD(T)] method and the augmented correlation consistent po-

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[†] Electronic Supplementary Information (ESI) available: The potential energy surface subroutine is provided. See DOI: 10.1039/cXCP00000x/

larized valence quadruple zeta (aug-cc-pVQZ) basis set. The interaction energy between CS and H₂ was obtained by subtracting the sum of the monomer potentials of CS and H₂ from the total energy of the CS-H₂ complex, where CS and H₂ were treated as rigid rotors with the bond length of H₂ fixed at its vibrationally averaged value, $r_0 = 1.4467 a_0$ in the vibrational ground state and the bond length of CS fixed at its equilibrium value ($r_e = 2.9006 a_0$). The PES was fitted with a least squares procedure for the angular terms and interpolation of the radial coefficients with cubic splines¹⁹. This 4D rigid rotor PES was applied to compute the rotational (de)excitation rate coefficients for the first 30 rotational levels of CS by collision with para-H₂ ($j_2=0$) and ortho-H₂ ($j_2=1$)^{13,14}. Additionally, the CS-para-H₂ rate coefficients obtained by mass-scaling the CS-He results of Lique et al.²¹ are also available in the Leiden Atomic and Molecular Database²³. These scaled results were also adopted by Neufeld et al.⁸ in their turbulent dissipation region models to determine the equilibrium level populations of CS in diffuse molecular clouds, where CS $j_1 = 2 - 1$ line was observed using the IRAM 30 m telescope. For CS vibrational excitation, Lique and Spielfiedel²² performed the scattering calculations of rovibrational excitation cross sections and rate coefficients of CS by He. However, to our knowledge, there are no theoretical results available for vibrational excitation of CS with H₂. The only available measurements are for the removal rate constants for vibrationally excited CS ($v_1 = 1$) with H₂, reported about a half century ago^{24,25}.

Quantum close-coupling (CC) calculations are the primary source of rate coefficients for astrophysical modeling. Full-dimensional quantum CC formalism has been developed^{26,27} for collisions involving two diatomic molecules. With the development of the quantum CC scattering code TwoBC²⁸, diatom-diatom systems in full-dimensionality can be treated and was first used for CC calculations of rovibrational collisions of H₂ with H₂²⁹⁻³². Rovibrational CC calculations were also performed for the collisional systems CO-H₂^{33,34}, CN-H₂³⁵, SiO-H₂³⁶, along with coupled-states approximation calculations in 5D and 6D³⁷⁻³⁹.

Here we report the first full-dimensional PES and the first vibrational inelastic scattering calculations for the CS-H₂ system. The paper is organized as follows. A brief description of the theoretical methods for the electronic structure and scattering calculations are given in Sec. 2. The results are presented and discussed in Sec. 3 followed by Astrophysical applications in Section 4. Section 5 summarizes the results and presents an outlook on future work.

2 Theoretical Methods

We briefly describe in this section the theoretical methods applied in the computation and analytical fit of the CS-H₂ PES as well as the quantum CC calculations in full dimensionality. The reader is referred to Refs. [30,33,40] for the details of the theoretical methodology.

2.1 Potential energy surface computation and fit

The interaction potential of CS-H₂ in the electronic ground state was computed on a 6D grid using Jacobi coordinates $(R, r_1, r_2, \theta_1, \theta_2, \phi)$. As shown in Fig. 1, R denotes the distance between the centers of mass of CS and H₂, and r_1 and r_2 are the bond lengths describing the vibration of CS and H₂, respectively. The angles θ_1 and θ_2 , respectively, are the in-plane orientation angles of \vec{r}_1 and \vec{r}_2 with \vec{R} while ϕ denotes the out-of-plane dihedral angle. The PES was computed with the MOLPRO suite of computational chemistry codes^{41,42}. The intermolecular distance R was chosen in the range of 4.5 - 25 a_0 and the bond distances are confined to $2.55 \leq r_1 \leq 3.51 a_0$ and $1.05 \leq r_2 \leq 2.27 a_0$. Here $a_0 = 0.529 \text{ \AA}$ is the Bohr radius. To produce an accurate 6D PES with proper symmetry the ab initio calculations were performed over the angular coordinates $0 \leq \theta_1 \leq 360^\circ$ and $0 \leq \theta_2, \phi \leq 180^\circ$, where $\theta_1 = \theta_2 = 0^\circ$ corresponds to the collinear configuration C-S-H-H.

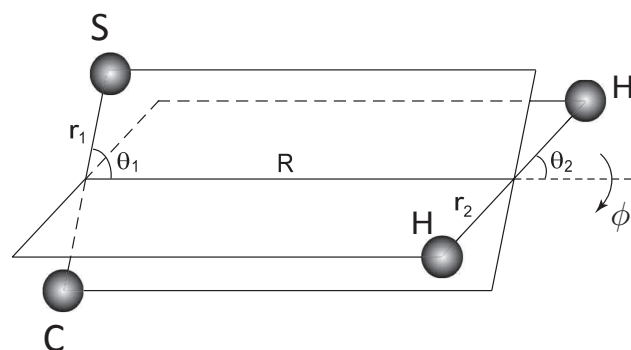


Fig. 1 The six-dimensional Jacobi coordinates for the CS-H₂ system.

The ab initio electronic structure computations of potential energies were performed using the explicitly correlated coupled-cluster (CCSD(T)-F12b) method^{43,44}. All the calculations employed aug-cc-pV5Z (for H and C atoms)⁴⁵ and aug-cc-pV(5+d)Z (for S atom) orbital basis set⁴⁶, and the corresponding MP2FIT (for H and C atoms) and aug-cc-pwCV5Z (for S atom) auxiliary bases^{47,48} for density fitting. The aug-cc-pV6Z-RI auxiliary bases (without k functions)⁴⁹ were used for the resolutions of the identify and density-fitted Fock matrices for all orbital bases. No scaled triples correction was used in the CCSD(T)-F12 calculation. The interaction PES was corrected for basis set superposition error (BSSE)⁵⁰ using the counter-poise (CP)⁵¹ method. Benchmark calculations at this CCSD(T)-F12 level were carried out on selected molecular configurations and results were compared with those from the conventional CCSD(T) method using aug-cc-pV5Z. The CP corrected interaction energy agrees closely with those derived from CCSD(T)/aug-cc-pV5Z.

The full-dimensional CS-H₂ interaction potential, referred to as VCSH2, is a hybrid one combining a fit to the full ab initio data set (denoted V_I) and a fit to the long-range data (denoted V_{II}) and is expressed by

$$V = (1 - s)V_I + sV_{II}, \quad (1)$$

the switching function s is given as

$$s = \begin{cases} 0 & (R < R_i) \\ 10b^3 - 15b^4 + 6b^5 & (R_i < R < R_f) \\ 1 & (R > R_f) \end{cases} \quad (2)$$

where $b = (R - R_i)/(R_f - R_i)$, $R_i = 8.5 a_0$ and $R_f = 10.5 a_0$ are the lower and upper bound of the switching region, respectively. Both V_I and V_{II} are expanded in the form

$$V_{I,II}(y_1 \cdots y_6) = \sum_{n_1 \cdots n_6} C_{n_1 \cdots n_6} y_1^{n_1} y_2^{n_2} y_3^{n_3} y_4^{n_4} y_5^{n_5} y_6^{n_6} (y_2^{n_2} y_3^{n_3} y_4^{n_4} y_5^{n_5} + y_2^{n_3} y_3^{n_2} y_4^{n_5} y_5^{n_4}) \quad (3)$$

and have been fitted in 6D using an invariant polynomial method^{40,52}, where $y_i = \exp(-d_i/p)$ are Morse-type variables and p is a user-specified parameter with $p = 2.0 a_0$ for V_I and $p = 7.0 a_0$ for V_{II} . The parameters d_i are the internuclear distances between two atoms and defined as $d_1 = d_{CS}$, $d_2 = d_{CH}$, $d_3 = d_{CH}$, $d_4 = d_{SH}$, $d_5 = d_{SH}$ and $d_6 = d_{HH}$. The powers n_1, \dots, n_6 satisfy $n_1 + \dots + n_6 \leq 7$ and $n_2 + n_3 + n_4 + n_5 \neq 0$, and the interaction potential is guaranteed to approach zero when CS and H₂ are infinitely far apart for all r_1 and r_2 . The total number of fitted linear coefficients $C_{n_1 \cdots n_6}$ is 882, and these coefficients were determined via linear least-squares fitting using the software MSA.⁵³ The root mean square (RMS) error in the long range fit V_{II} is 0.062 cm^{-1} , for V_I the RMS error is 14.2 cm^{-1} .

In Fig. 2 the R dependence of VCSH2 PES is compared with the PES of Denis-Alpizar et al.²⁰ for $(\theta_1, \theta_2, \phi) = (0^\circ, 0^\circ, 0^\circ)$, $(180^\circ, 0^\circ, 0^\circ)$, $(180^\circ, 90^\circ, 0^\circ)$, and $(90^\circ, 90^\circ, 90^\circ)$. Good agreement between our PES and the PES of Denis-Alpizar et al.²⁰ is displayed, except that our PES is a little shallower at the global minimum. Our fitted PES has a depth of -162.56 cm^{-1} at the collinear structure with the C atom towards to H₂ and $R = 8.6 a_0$. The minimum of the PES of Denis-Alpizar et al.²⁰ is about -173 cm^{-1} and also corresponds to a collinear geometry with same R value. Fig. 3 shows a two-dimensional contour plot of the VCSH2 PES in θ_1, θ_2 space for fixed values of $r_1 = 2.9006 a_0$, $r_2 = 1.4011 a_0$, $R = 8.5 a_0$, and $\phi = 0^\circ$.

2.2 Scattering Calculation

The full-dimensional quantum CC scattering calculations were performed using the TwoBC code²⁸. To facilitate the scattering calculations, it is convenient to expand the angular dependence of the interaction potential between CS and H₂, $V(\vec{r}_1, \vec{r}_2, \vec{R})$ at each intermolecular distance R according to⁵⁴,

$$V(R, r_1, r_2, \theta_1, \theta_2, \phi) = \sum_{\lambda_1 \lambda_2 \lambda_{12}} A_{\lambda_1 \lambda_2 \lambda_{12}}(r_1, r_2, R) Y_{\lambda_1 \lambda_2 \lambda_{12}}(\hat{r}_1, \hat{r}_2, \hat{R}), \quad (4)$$

where the bi-spherical harmonic function is expressed as,

$$Y_{\lambda_1 \lambda_2 \lambda_{12}}(\hat{r}_1, \hat{r}_2, \hat{R}) = \sum_{m_{\lambda_1} m_{\lambda_2} m_{\lambda_{12}}} \langle \lambda_1 m_{\lambda_1} \lambda_2 m_{\lambda_2} | \lambda_{12} m_{\lambda_{12}} \rangle \times Y_{\lambda_1 m_{\lambda_1}}(\hat{r}_1) Y_{\lambda_2 m_{\lambda_2}}(\hat{r}_2) Y_{\lambda_{12} m_{\lambda_{12}}}^*(\hat{R}). \quad (5)$$

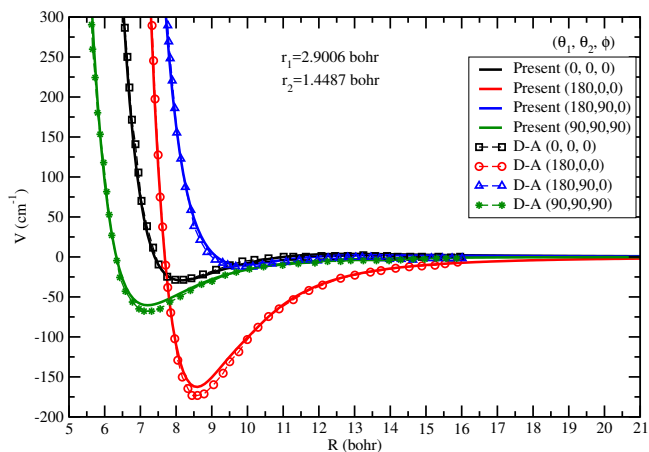


Fig. 2 The R dependence of the CS-H₂ interaction potential, VCSH2 for $(\theta_1, \theta_2, \phi) = (0^\circ, 0^\circ, 0^\circ)$, $(180^\circ, 0^\circ, 0^\circ)$, $(180^\circ, 90^\circ, 0^\circ)$, and $(90^\circ, 90^\circ, 90^\circ)$. The bond lengths of CS and H₂ are fixed at equilibrium value and vibrationally averaged value in the rovibrational ground state, respectively. Symbols are for the PES of Denis-Alpizar et al.²⁰ (D-A).

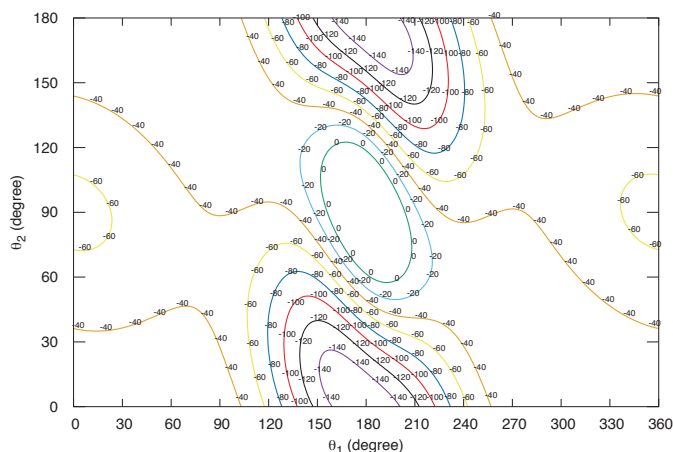


Fig. 3 Contour plots of the potential VCSH2 as a function of θ_1 and θ_2 for $r_1 = 2.9006 a_0$, $r_2 = 1.4011 a_0$, $R = 8.5 a_0$, and $\phi = 0^\circ$.

Terms $0 \leq \lambda_1 \leq 8$ and $0 \leq \lambda_2 \leq 4$ are retained in the expansion. Only even values of λ_2 contribute because H₂ is homonuclear.

We use a combined molecular state (CMS)³⁰ notation, $(v_1 j_1 v_2 j_2)$, to describe a combination of rovibrational states for CS $(v_1 j_1)$ and H₂ $(v_2 j_2)$, where j_i and v_i ($i = 1, 2$) are the rotational and vibrational quantum numbers of CS and H₂. For a rovibrational transition the state-to-state cross section can be obtained as a function of the collision energy E_c from the corresponding scattering matrix S :

$$\begin{aligned} \sigma_{v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2}(E_c) &= \frac{\pi}{(2j_1 + 1)(2j_2 + 1)k^2} \\ &\times \sum_{j_{12} j'_{12} l l' J \mathcal{E}_l} (2J + 1) |\delta_{v_1 j_1 v_2 j_2, v'_1 j'_1 v'_2 j'_2} \\ &- S_{v_1 j_1 v_2 j_2, v'_1 j'_1 v'_2 j'_2}^{J \mathcal{E}_l}(E_c)|^2, \end{aligned} \quad (6)$$

where the wave vector $k = \sqrt{2\mu E_c/\hbar^2}$ and the primed quantities refer to the final state. The quantum number J denotes the total angular momentum, $\vec{J} = \vec{l} + \vec{j}_{12}$, with $\vec{j}_{12} = \vec{j}_1 + \vec{j}_2$ and l is the orbital angular momentum quantum number.

The total quenching cross section of CS from initial state $(v_1 j_1 v_2 j_2) \rightarrow (v'_1; v'_2 j'_2)$ is obtained by summing the state-to-state quenching cross sections over the final rotational state of j'_1 of CS in vibrational state v'_1 ,

$$\sigma_{v_1 j_1 v_2 j_2 \rightarrow v'_1; v'_2 j'_2}(E_c) = \sum_{j'_1} \sigma_{v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2}(E_c). \quad (7)$$

From the state-to-state cross section $\sigma_{v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2}$ the thermal rate coefficients at a temperature T can be obtained by thermally averaging over collision energy (E_c).

$$\begin{aligned} k_{v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2}(T) &= \left(\frac{8}{\pi \mu \beta} \right)^{1/2} \beta^2 \\ &\times \int_0^\infty E_c \sigma_{v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2}(E_c) \exp(-\beta E_c) dE_c, \end{aligned} \quad (8)$$

where μ is the reduced mass of the CS-H₂ system, $\beta = (k_B T)^{-1}$, and k_B is Boltzmann's constant.

In the full-dimensional rovibrational scattering calculations with the TwoBC code²⁸ the log-derivative matrix propagation method of Johnson⁵⁵ was employed to propagate the CC equations from $R = 4.5 a_0$ to $25 a_0$. The number of Gauss-Hermite quadrature points N_{r_1} , N_{r_2} ; the number of Gauss-Legendre quadrature points in θ_1 and θ_2 , N_{θ_1} , N_{θ_2} ; and the number of Chebyshev quadrature points in ϕ , N_ϕ adopted to project out the expansion coefficients of the PES are listed in Table 1. In the scattering calculations, the monomer potentials of Paulose et al.⁵⁶ and Schwenke⁵⁷ are used to describe the rovibrational motions of CS and H₂, respectively.

3 Results and Discussion

3.1 Pure rotational de-excitation

The rotational de-excitation cross sections of CS ($v_1=0$, j_1) in collision with H₂ have been calculated for the transitions, CS($v_1=0$,

j_1) + H₂($v_2=0$, j_2) \rightarrow CS($v'_1=0$, j'_1) + H₂($v'_2=0$, j'_2), where both CS and H₂ are taken to be in their ground vibrational states, i.e., $(0 j_1 0 j_2) \rightarrow (0 j'_1 0 j'_2)$. We performed the calculations in full-dimension for the initial rotational states of CS $j_1 = 1 - 5$, with collision energy ranging from 1 to 3000 cm⁻¹. Sufficient number of partial waves were included to ensure the convergence of the cross sections. Convergence tests were also made with respect to the para-H₂ basis, it was found that the effect from inclusion of the $j_2 = 4$ state is generally less than 1%. The basis sets and partial waves used in the scattering calculations are provided in Table 1. In Fig. 4 the state-to-state quenching cross sections of CS from initial state $j_1=5$ from our calculations are compared with the results of Denis-Alpizar et al.¹³. Results are presented for both para-H₂ ($j_2=0$) and ortho-H₂ ($j_2 = 1$) for final states $j'_1=0, 1, 2, 3$, and 4. Fig. 4(a) shows that for para-H₂, for collision energies below ~ 30 cm⁻¹, all state-to-state cross sections display resonances due to the decay of quasibound states supported by the van der Waals well of the PES. At collision energies below 200 cm⁻¹, the cross sections generally increase with increasing j'_1 with the smallest cross section corresponding to the $j_1 = 5 \rightarrow 0$ transition, i.e., the largest $|\Delta j_1 = j'_1 - j_1|$. While for collision energies above 200 cm⁻¹ the state-to-state quenching cross sections are dominated by $\Delta j_1 = -2$ transitions. Above ~ 1000 cm⁻¹, the cross sections for $j_1 = 5 \rightarrow 1$ becomes larger than $j_1 = 5 \rightarrow 2$. The agreement between our results and the results of Denis-Alpizar et al.¹³ is reasonable, though differences are seen in the low collision energy region due to the presence of scattering resonances. These differences tend to disappear as the collision energy is increased. One exception is the transition $j_1 = 5 \rightarrow 0$, where good agreement is only obtained for collision energies between 150 and 500 cm⁻¹, but these cross sections have the smallest magnitude. For ortho-H₂, as Fig. 4(b) depicts, the state-to-state cross sections exhibit similar trend as for para-H₂. The energy gap law is more pronounced here with a decrease of the cross section with increase in $|\Delta j_1|$. However, the resonance features are almost absent, presumably due to the broader range of partial waves involved. The quenching cross sections are dominated by $\Delta j_1 = -1$ transition for collision energies below ~ 1000 cm⁻¹, followed by $\Delta j_1 = -2$. Except for the $j_1 = 5 \rightarrow 0$ transition at low collision energies, our results are in very good agreement with the results of Denis-Alpizar et al.¹³.

Fig. 5 (a) and (b) display the total rotational quenching cross sections from initial states $j_1 = 1 - 5$ of CS with para-H₂ ($j_2 = 0$) and ortho-H₂ ($j_2 = 1$), respectively. It is found that for both para-H₂ and ortho-H₂, except for collision energies below ~ 3 cm⁻¹, the total rotational quenching cross sections increase with increasing initial j_1 . For para-H₂, the resonance features observed in the state-to-state cross sections can also be noted in the total quenching cross sections, particularly in the $j_1 = 1$ state.

In Fig. 6, we provide a comparison between the para-H₂ and ortho-H₂ cross sections for initial rotational states $j_1=1$ and 2. For $\Delta j_1 = -1$, the cross section of ortho-H₂ are larger than that of para-H₂ over the whole range of collision energy. While for the $j_1 = 2 \rightarrow 0$ transition, the cross sections of para-H₂ and ortho-H₂ are of comparable magnitude, though the resonance dominated region for para-H₂ shows significant differences.

Table 1 Parameters used in the scattering calculations.

Basis set		$N_{\theta_1}(N_{\theta_2})$	N_{ϕ}	$N_{r_1}(N_{r_2})$	λ_1	λ_2	
6D Rotation							
para-H ₂ -CS	$j_1^{\max} = 30, j_2 = 0, 2$	12	8	18	8	4	(16, 30, 80, 160) ^b
ortho-H ₂ -CS	$j_1^{\max} = 30, j_2 = 1, 3$	12	8	18	8	4	(18, 32, 82, 162) ^b
6D Rovibration							
para-H ₂ -CS	[(0,35;1,20)(0,2)] ^a	12	8	18	8	4	(16, 30, 80, 160) ^b
ortho-H ₂ -CS	[(0,35;1,20)(0,3)] ^a	12	8	18	8	4	(18, 32, 82, 162) ^b

^a Basis set $[(v_1 = 0, j_{v_1=0}^{\max}; v_1 = 1, j_{v_1=1}^{\max})(v_2 = 0, j_{v_2=0}^{\max})]$ is presented by the maximum rotational quantum number $j_{v_1}^{\max}$ and $j_{v_2}^{\max}$ included in each relevant vibrational level v_1 and v_2 for CS and H₂, respectively.

^b Maximum partial waves $J(J_{E_1}, J_{E_2}, J_{E_3}, J_{E_4})$ used in scattering calculations for collision energies $E_1=10, E_2=100, E_3=1000,$ and $E_4=3000 \text{ cm}^{-1}$, respectively.

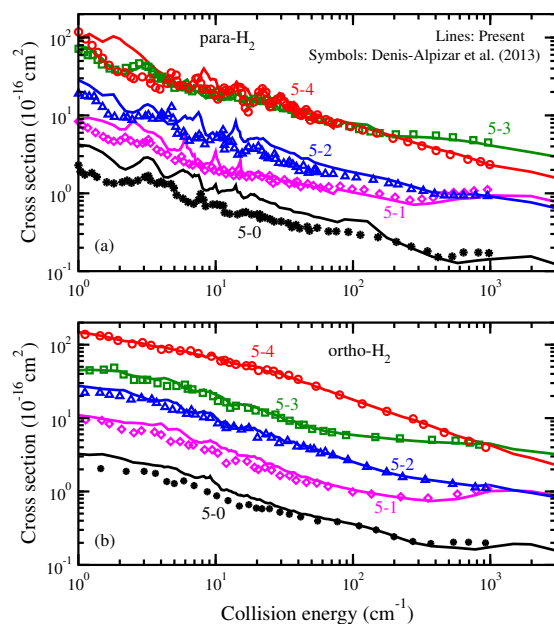


Fig. 4 Rotational state-to-state de-excitation cross sections for $\text{CS}(j_1) + \text{H}_2(j_2) \rightarrow \text{CS}(j_1') + \text{H}_2(j_2')$, $j_1 = 5, j_1' < j_1$. Lines are for the present results and symbols are for the results of Denis-Alpizar et al.¹³. (a) CS in collision with para-H₂, $j_2 = j_2' = 0$; (b) CS in collision with ortho-H₂, $j_2 = j_2' = 1$.

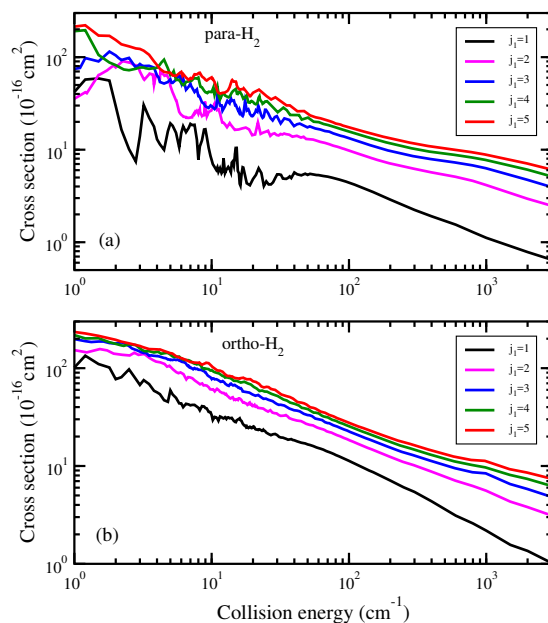


Fig. 5 Total rotational de-excitation cross sections for $\text{CS}(j_1)$ from initial states $j_1=1, 2, 3, 4,$ and 5 . (a) CS in collision with para-H₂, $j_2 = j_2' = 0$; (b) CS in collision with ortho-H₂, $j_2 = j_2' = 1$.

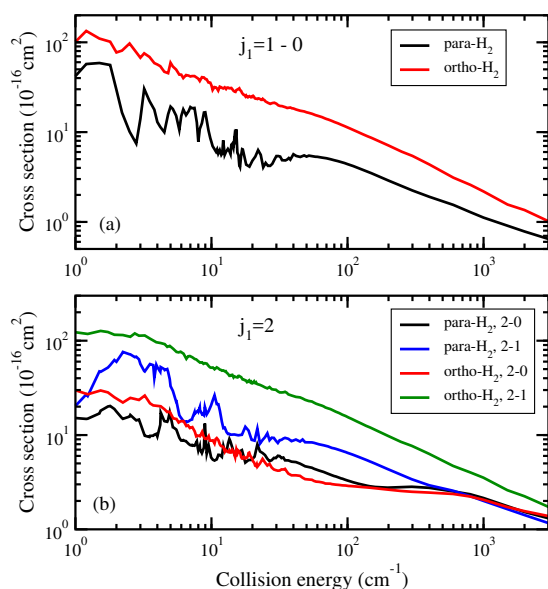


Fig. 6 Comparison of the rotational state-to-state de-excitation cross sections for CS in collision with para- and ortho-H₂. (a) from initial state $j_1=1$; (b) from initial state $j_1=2$.

In Figs. 7 (a) and (b) we show the temperature dependence of the rate coefficients for rotational quenching of CS from $j_1 = 2$ induced by para- and ortho-H₂ collisions, respectively, in the temperatures range of 5 to 600 K. For comparison, the corresponding rate coefficients of Denis-Alpizar et al.¹⁴ are also included. The temperature dependence is the steepest for the $j_1 = 2 \rightarrow 0$ rate coefficient for para-H₂ collisions. While for $j_1 = 2 \rightarrow 1$, the rate coefficient first decreases with temperature from $T = 5 \text{ K} \sim 20 \text{ K}$, then increases gradually with increasing temperature. Compared to the results of Denis-Alpizar et al.¹⁴, good agreement is observed for the $j_1 = 2 \rightarrow 0$ rate coefficients. However, for the $j_1 = 2 \rightarrow 1$ transition, our rate coefficient is larger than the results of Denis-Alpizar et al. but the differences tend to vanish as the temperature is increased. As shown in Fig. 2, the VCSH2 PES and the PES of Denis-Alpizar et al.²⁰ have different well depths with VCSH2 being the shallower one. This leads to different resonance structures in the cross sections on the two PESs, particularly, at low collision energies. The differences in the rate coefficients at low temperatures may be attributed to the different resonance structures. Figure 8 provides a comparison of the state-to-state rate coefficients from the present work for $j_1 = 5$ with that of Denis-Alpizar et al.¹⁴. The para-H₂ results shown in Fig. 8(a) are in reasonable agreement with the results of Denis-Alpizar et al. while the ortho-H₂ results presented in Fig. 8(b) are in excellent agreement.

When rate coefficients for a particular collision complex are lacking, it has been argued that rate coefficients from chemically similar systems could be adopted⁵⁸. We test this idea by comparing the current results from CS to prior work on SiO³⁶ and SiS^{59,60}. In Fig. 9, the state-to-state rate coefficients for rotational quenching from initial state $j_1 = 3$ for para-H₂ collisions are shown. The rate coefficients differ by a factor of ~ 5 with no clear trend. Adoption of such an approximation is clearly not

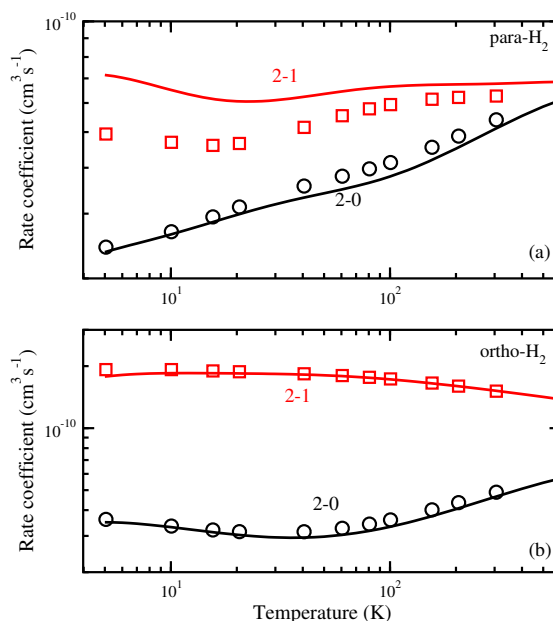


Fig. 7 Rotational state-to-state de-excitation rate coefficients compared with the results of Denis-Alpizar et al. (D-A)¹⁴ for CS($j_1=2$) in collision with (a) para-H₂($j_2=0$) and (b) ortho-H₂($j_2=1$).

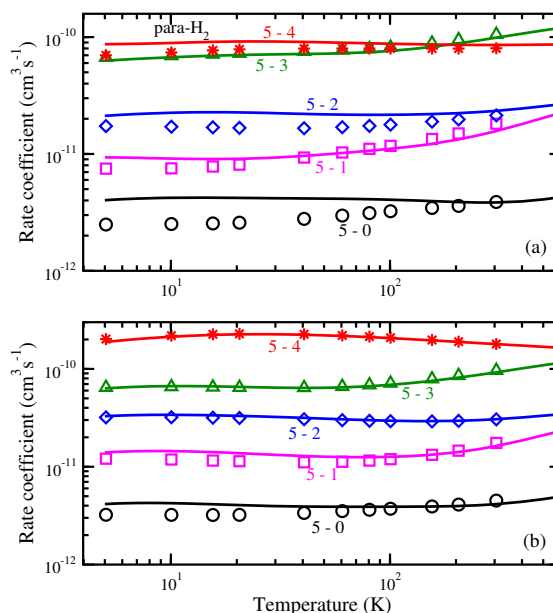


Fig. 8 Rotational state-to-state de-excitation rate coefficients compared with D-A for CS($j_1=5$) in collision with (a) para-H₂($j_2=0$) and (b) ortho-H₂($j_2=1$).

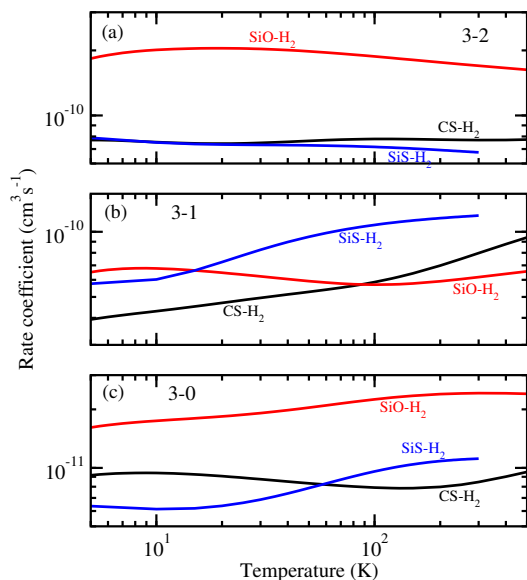


Fig. 9 Rotational state-to-state de-excitation rate coefficients from initial $j_1=3$ of CS, SiO, and SiS in collisions with para- $\text{H}_2(j_2=0)$. (a) $j_1 = 3 \rightarrow 2$, (b) $j_1 = 3 \rightarrow 1$, (c) $j_1 = 3 \rightarrow 0$.

advisable.

3.2 Vibrational quenching

Here we present close-coupling calculations of rovibrational transitions in CS due to H_2 collisions in full-dimensionality, the main focus of this work.

The state-to-state quenching cross sections were computed for CS rovibrational transitions from $v_1=1$, $\text{CS}(v_1=1, j_1)+\text{H}_2(v_2=0, j_2) \rightarrow \text{CS}(v_1'=0, j_1') + \text{H}_2(v_2'=0, j_2')$, i.e., $(1 j_1 0 j_2) \rightarrow (1 j_1' 0 j_2')$. In our calculations, initial $j_1=0-5$ and final $j_1'=0, 1, 2, \dots, 35$. For para- H_2 , $j_2=0, j_2'=0$ and 2, while for ortho- H_2 , $j_2=1, j_2'=1$ and 3 are considered. We only consider the rotational excitations of H_2 within its ground vibrational state, i.e., $v_2=v_2'=0$ for all of the results presented here. The basis sets employed in the scattering calculations are given in Table 1. All vibrational quenching cross sections were calculated for collision energies between 1 and 3000 cm^{-1} .

As examples, we show in Fig. 10 the state-to-state quenching cross sections from initial CMS (1000) and (1001) into selected final rotational states in $v_1'=0, j_1'=0, 2, 4, 6, 8, 10, 15, 20$, and 25. These results correspond to rotationally elastic scattering of the H_2 molecule, i.e., $j_2=0 \rightarrow j_2'=0$. As seen from Fig. 10, for both para- H_2 and ortho- H_2 colliders, a large number of resonances are observed in the cross sections at collision energies between 1 and 50 cm^{-1} . We also notice that the resonances persist to higher energies with increasing j_1' . Additionally, the state-to-state quenching cross sections increase with collision energy for energies above $\sim 50 \text{ cm}^{-1}$. Overall, the cross sections corresponding to $j_1' \leq 15$ show similar resonance structures and exhibit similar energy dependence. The cross sections for $j_1'=20$ and 25 are about two to three orders of magnitude smaller than other transitions for both para- and ortho- H_2 for collision energies below 300 cm^{-1} , however they increase rapidly with energy, and

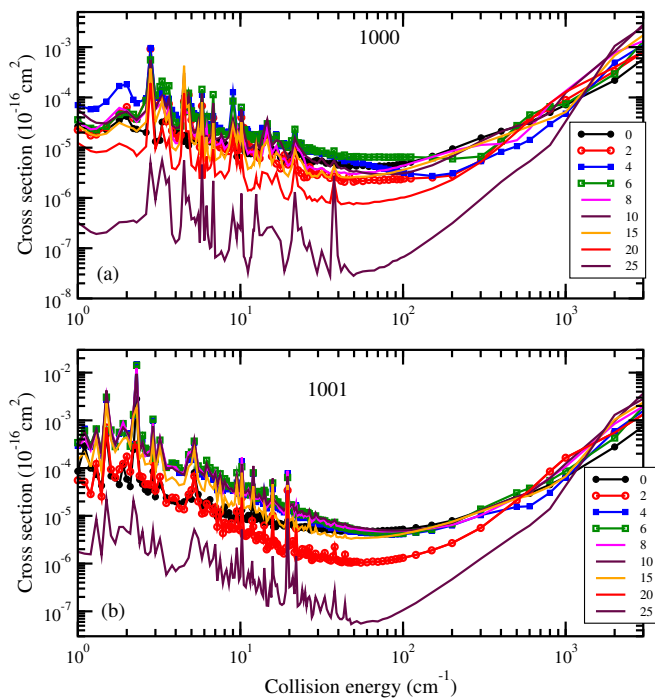


Fig. 10 Vibrational state-to-state quenching cross section for transitions $\text{CS}(v_1=1, j_1=0) + \text{H}_2(j_2) \rightarrow \text{CS}(v_1'=0, j_1') + \text{H}_2(j_2)$, $j_1'=0, 2, 4, 6, 8, 10, 15, 20$, and 25. (a) para- $\text{H}_2(j_2=0)$ and (b) ortho- $\text{H}_2(j_2=1)$.

the cross section of $j_1'=25$ becomes the largest at an energy of 3000 cm^{-1} .

Next we discuss the effect of vibrational excitation of CS on its pure rotational quenching. This is provided in Fig.11 for $v_1=0$ and 1 for rotational levels $j_1=1$ and 5 to all $j_1' < j_1$ for para- H_2 with H_2 scattered elastically. It can be seen that the cross sections are nearly identical for $v_1=0$ and 1, over the whole range of energies considered in this work demonstrating the negligible effect of vibrational excitation of CS on pure rotational quenching. This is due to the almost harmonic nature of the $v=0$ and 1 vibrational levels of CS. Similar results are found for ortho- H_2 collisions. This also means that, effect of vibrational excitation of CS can be ignored for pure rotational transitions in CS in collisions with ortho- and para- H_2 , at least for low vibrational levels. A similar conclusion was also drawn for the SiO- H_2 system³⁶.

Using Eq. 7 the total vibrational quenching cross section of CS from initial CMS (1000) and (1001) was obtained by summing the state to state quenching cross sections over the final rotational state j_1' of CS in vibrational state $v_1=0$. These total quenching cross section were calculated for elastic and inelastic transitions in H_2 .

Fig. 12 (a) presents the energy dependence of the total $v_1=1 \rightarrow v_1'=0$ quenching cross section with para- H_2 from CMSs (1000) for elastic ($j_2=0 \rightarrow j_2'=0$) and inelastic ($j_2=0 \rightarrow j_2'=2$) transitions in H_2 . While they exhibit similar energy dependencies and similar resonance structures at low energies, the cross sections for elastic transition in H_2 are about a factor of two larger than its inelastic counterpart in the entire energy range. For ortho- H_2 and initial CMS (1001), Fig. 12 (b) shows that the total vibrational quenching cross sections for elastic ($j_2=1 \rightarrow j_2'=1$) and

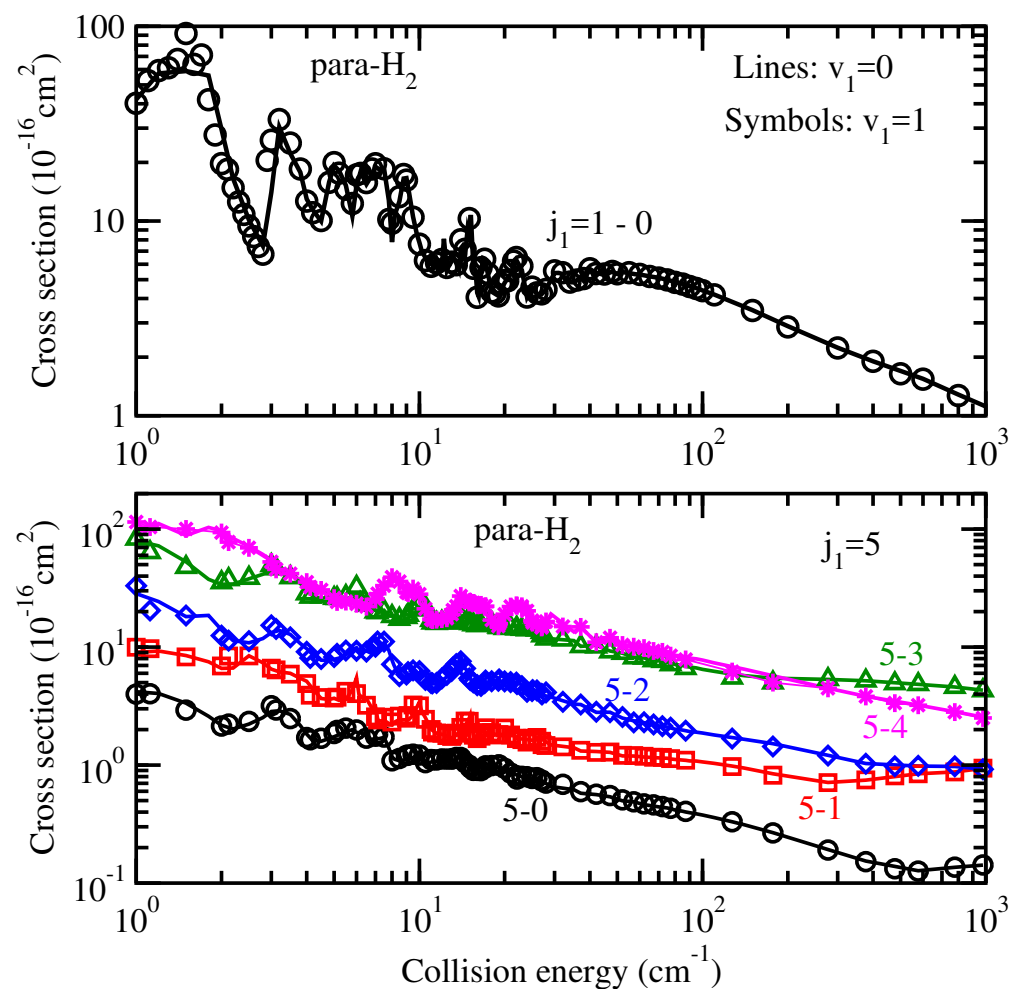


Fig. 11 Rotational quenching state-to-state excitation cross section of CS from initial states $j_1=1$ and 5 to $j'_1, j'_1 < j_1$. (a) and (b): para- H_2 . For each transition, the comparison is made between $v_1 = 0$ and $v_1 = 1$.

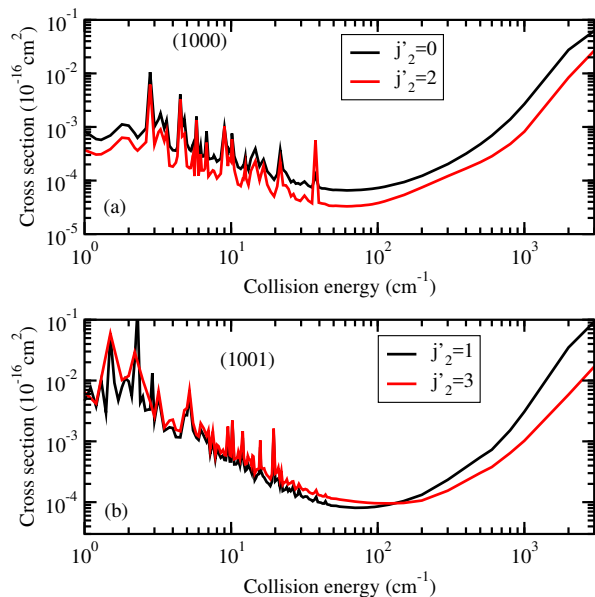


Fig. 12 Total vibrational quenching cross section for transitions $\text{CS}(v_1=1, j_1) + \text{H}_2(j_2) \rightarrow \text{CS}(v_1'=0) + \text{H}_2(j_2)$. $j_1=0$. (a) para- $\text{H}_2(j_2=0)$. (b) ortho- $\text{H}_2(j_2=1)$.

inelastic ($j_2 = 1 \rightarrow j_2' = 3$) transitions in H_2 are comparable for collision energies below $\sim 200 \text{ cm}^{-1}$. For energies above $\sim 200 \text{ cm}^{-1}$, the cross section for H_2 rotation preserving transition becomes increasingly dominant.

We also calculated the state-to-state and total vibrational quenching rate coefficients of $\text{CS}(v_1=1, j_1)$ in collisions with para- $\text{H}_2(j_2=0)$ and ortho- $\text{H}_2(j_2=1)$ for $j_1=0-5$. State-to-state rate coefficients are obtained for $j_1'=0, 1, 2, \dots, 35$ and $j_2'=0$ and 2 for para- H_2 and $j_2'=1$ and 3 for ortho- H_2 . Unfortunately, there are no published experimental or theoretical state-to-state rate coefficients available for comparison. As an example, in Fig. 13 we show the total vibrational quenching rate coefficients for temperatures between 1 and 600 K for CMS (1000) to $(v_1'=0)$ and $j_2'=0$, and CMS (1001) to $(v_1'=0)$ and $j_2'=1$.

Previously we have provided a comparison of CS- H_2 rate coefficients with that of CO- H_2 (Ref.33) and for SiO- H_2 (Ref.36). It was shown that for the same transitions, the total quenching rate coefficients of CO- H_2 are typically ~ 2 -3 orders of magnitude smaller than that of CS- H_2 and SiO- H_2 . The large magnitude of SiO- H_2 rate coefficients are likely due to the high anisotropy of the SiO- H_2 PES. Interestingly, at high temperatures the CS- H_2 rate coefficients merge with those of SiO- H_2 . Furthermore, generally the rate coefficients increase with increasing well depth of the interaction PES, the SiO- H_2 rate coefficients are largest with a well depth of 293.2 cm^{-1} and CO- H_2 rate coefficients are smallest with a well depth of 93.1 cm^{-1} .

4 Astrophysical Applications

A quantitative non-LTE modeling of molecular excitation and line formation processes from infrared and submillimetre observations requires detailed knowledge of collisional rate coefficients for transitions between the rovibrational states of molecules over a wide range of levels and temperatures. Molecular collisions,

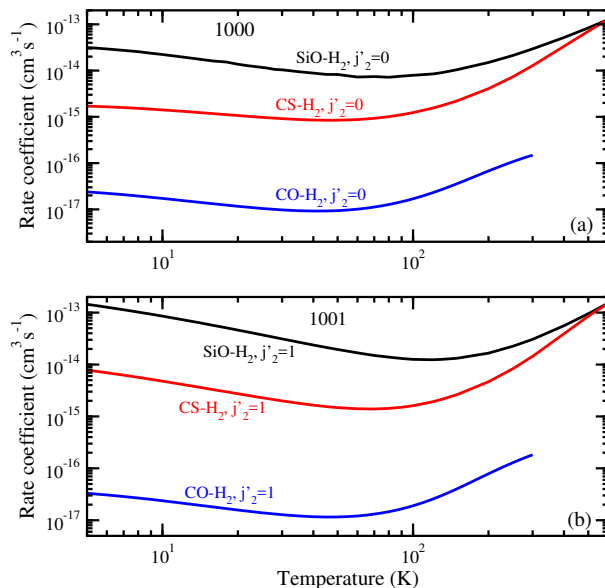


Fig. 13 Total rate coefficients for the vibrational quenching of CS compared to the same transitions for CO from Ref. [33] and SiO from Ref. [36]. (a) from (1000) to $v_1'=0 + \text{para-H}_2(v_2'=0, j_2'=0)$. (b) from (1001) to $v_1'=0 + \text{ortho-H}_2(v_2'=1, j_2'=1)$.

which are responsible for most of the excitation and reaction processes, are important in the interstellar medium (ISM). Particularly, in cold molecular clouds, collisional processes are the dominant factor in analysis of emission and absorption spectra, and H_2 and He are the most important collision partners due to their large abundances, except in photodissociation regions (PDRs) and diffuse gas where collisions with electrons and H can become important. However, direct measurements of the collisional rate coefficients are difficult and complicated; astrophysical modeling heavily rely on theoretical calculations⁶¹.

Carbon monosulfide and its isotopic species have been detected in a large range of astrophysical environments. As a high-density tracer of dense gas, CS emission is normally used in the study of star forming regions. Using the IRAM Plateau de Bure interferometer Guilloteau et al.⁶² observed two CS transitions $j_1 = 3-2$ and $j_1 = 5-4$ in the DM Tau disk. The line intensities were used to determine the magnitude of the turbulent motions in the outer parts of the disk. Maxted et al.⁶³ detected emission $j_1 = 1-0$ and $j_1 = 2-1$ of CS and its isotopologues in four of the densest cores towards the western rim of supernova remnant RX J1713.7-3946 and confirmed the presence of dense gas $\geq 10^4 \text{ cm}^{-3}$ in the region. More recently, CS emission (1-0) was used in the investigation of the nature of the supernova remnant HESS J1731-347⁶⁴. Line emission from rotational transition $j_1 = 7-6$ within the vibrationally excited state $v = 1$ was observed in IRAS 16293-2422⁶⁵. Gómez-Ruiz et al.⁶⁶ detected CS and isotopologues $^{12}\text{C}^{32}\text{S}$, $^{12}\text{C}^{34}\text{S}$, $^{13}\text{C}^{32}\text{S}$, $^{12}\text{C}^{33}\text{S}$, for a total of 18 transitions with Herschel/HIFI and IRAM-30m at L1157-B1. With Herschel/HIFI spectral line survey⁶⁷ CS transitions were detected toward the Orion Bar, tracing the warm and dense gas with temperatures of 100-150 K and densities of $10^5 - 10^6 \text{ cm}^{-3}$. NLTE analysis was also performed with RADEX, where the CS- H_2 rate coefficients

were obtained by reduced-mass scaling the rate coefficients with He of Lique et al.²¹ Using the IRAM 30 m telescope, Aladro et al.⁶⁸ performed a molecular line survey towards the circumnuclear regions of eight active galaxies, CS and its isotopologues were identified in M83, M82, M51, and NGC 253. Using the Atacama Large Millimeter/submillimeter Array (ALMA), Takano et al.⁶⁹ performed a high resolution imaging study of molecular lines near the supermassive black hole at the center of galaxy NGC 1068. CS emission of $j_1 = 2 - 1$ was distributed both in the circumnuclear disk and the starburst ring. Walter et al.⁷⁰ investigated dense molecular gas tracers in the nearby starburst galaxy NGC 253 using ALMA, CS ($j_1 = 2 - 1$) was detected in the molecular outflow.

Vibrationally excited molecules, which are excited by collision or infrared radiation, can be used to probe extreme physical conditions with high gas densities and temperatures. The first observation of vibrationally excited CS in the circumstellar shell of IRC + 10216 was reported by Turner⁷¹ through transitions $j_1 = 2 \rightarrow 1$ and $5 \rightarrow 4$ in $v_1 = 1$. In 2000, Highberger et al.⁷² reobserved these lines and also detected new transitions of $j_1 = 3 - 2$, $6 - 5$, and $7 - 6$ of vibrationally excited CS ($v = 1$) toward IRC+10216. Using Submillimeter Array, Patel et al.⁷³ detected the CS $v_1 = 2$, $j_1 = 7 - 6$ transition from the inner envelope of IRC+10216. Finally, vibrational absorption lines for CS have been detected for its fundamental band near $8 \mu\text{m}$ in IRC +10216⁷⁴. These observations used the Texas Echelon-cross-Eschelle Spectrograph (TEXES) on the 3 m Infrared Telescope facility.

Our present full-dimensional scattering calculation will be able to provide accurate rovibrational state-to-state CS-H₂ collisional data for future modeling of protostars, the infrared sources discussed above, and future FIR and submillimeter observations with Herschel and ALMA. Furthermore, CS vibrational bands in the $1\text{-}5 \mu\text{m}$ region will be accessible by the James Webb Space Telescope (JWST) to be launched in 2021 and currently with SOFIA using the the EXES ($5\text{-}28 \mu\text{m}$) or FORCAST ($5\text{-}40 \mu\text{m}$) instruments. In PPDs, CS vibrational lines probe the inner warm regions which are exposed to the UV radiation from the protostar.

5 Summary

We constructed a 6-dimensional potential energy surface for CS-H₂ based on high-level electronic structure calculations. State-to-state cross sections for rotational and rovibrational transitions in CS in collisions with H₂ are reported using full-dimensional quantum scattering calculations and an analytical fit of the potential surface.

Cross sections and rate coefficients for pure rotational transitions from the present study are found to be in good agreement with the rigid-rotor approximation calculations of Denis-Alpizar et al.^{13,14} using a 4-dimensional potential surface. The vibrational quenching cross sections and rate coefficients have been reported for the first time. In future work, we plan to extend the current calculations to higher rotational and vibrational states of CS and include the effect of vibrational excitation of the H₂ molecule.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Work at UGA and Emory was supported by NASA grant NNX16AF09G, at UNLV by NSF Grant No. PHY-1505557, and at Penn State by NSF Grant No. PHY-1503615. This study was supported in part by resources and technical expertise from the UGA Georgia Advanced Computing Resource Center (GACRC), and UNLV National Supercomputing Institute & Dedicated Research Network. We thank Shan-Ho Tsai (GACRC), Jeff Deroshia (UGA Department of Physics and Astronomy), and Ron Young (UNLV) for computational assistance.

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