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Research paper

# Fine-structure resolved rotational transitions and database for $\rm CN+H_2$ collisions



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#### ABSTRACT

Cross sections and rate coefficients for  $CN + H_2$  collisions are calculated using the coupled states (CS) approximation. The calculations are benchmarked against more accurate close-coupling (CC) calculations for transitions between low-lying rotational states. Comparisons are made between the two formulations for collision energies greater than  $10 \text{ cm}^{-1}$ . The CS approximation is used to construct a database which includes highly excited rotational states that are beyond the practical limitations of the CC method. The database includes fine-structure resolved rotational quenching transitions for v = 0 and  $j \le 40$ , where v and j are the vibrational and rotational quantum numbers of the initial state of the CN molecule. Rate coefficients are computed for both para-H<sub>2</sub> and ortho-H<sub>2</sub> colliders. The results are shown to be in good agreement with previous calculations, however, the rates are substantially different from mass-scaled CN+He rates that are often used in astrophysical models.

#### 1. Introduction

H<sub>2</sub> and CO are the most abundant molecules in the majority of interstellar environments, while CN has been detected in a variety of molecular clouds (Guilloteau, 2013; Hily-Blant, 2013; Mookerjea, 2014; Ritchey et al., 2013; Wootten et al., 1982) and is believed to be a good tracer of high density gas. When these environments are exposed to intense UV radiation, the chemistry and internal level populations of the gas are driven out of equilibrium, and it is necessary to include detailed rate coefficients for a variety of collision processes in models which aim to interpret the infrared emission from the molecules. Examples where such detailed information is needed include photodissociation regions (PDRs) which reside at the interface between hot ionized hydrogen (HII) and cold molecular regions, and protoplanetery disks (PPDs) of young stellar objects. Reliable models of these environments require an extensive set of state-to-state rate coefficients for rovibrational transitions induced by H<sub>2</sub> collisions. Due to the fundamental and astrophysical importance of CN+H<sub>2</sub>, there have been a number of experimental (Brunet et al., 2002; O'Donnell et al., 2012) and theoretical (Flower and Lique, 2015; Horst et al., 1996; Kalugina et al., 2013; Kalugina and Lique, 2015; Kalugina et al., 2012) studies reported in the literature. Many of these studies focused on the formation of the HCN molecule, however, several were interested in the collision-induced rotational transitions of CN, including transitions

which resolve the fine-structure (Kalugina et al., 2013) and hyperfine structure (Flower and Lique, 2015; Kalugina and Lique, 2015; Kalugina et al., 2012). These papers reported cross sections and rate coefficients obtained from close-coupling (CC) calculations using a four-dimensional PES with the diatomic molecules fixed at their average or equilibrium distances. The rate coefficients (Kalugina et al., 2013) were shown to be in good agreement with the limited amount of experimental data (Brunet et al., 2002) that are available for rotational transitions. The hyperfine results (Kalugina and Lique, 2015; Kalugina et al., 2012) for para-H2 were also compared to mass-scaled CN+He data (Lique and Klos, 2011). Significant discrepancies were observed in these comparisons due to the inadequacy of mass-scaling approximations (Walker et al., 2014). Nevertheless, the rotational rate coefficients that are currently available on the widely-used Leiden Atomic and Molecular Database (LAMDA) website (Schöier et al., 2005) are obtained from mass-scaled CN+He results (Lique et al., 2010). The present paper describes a database which aims to improve these rate coefficients and extend the data available on the LAMDA and BASECOL (Dubernet, 2013) websites to higher rotational levels and temperatures.

The database is constructed by numerically solving the Schrödinger equation using the five dimensional coupled states (5D-CS) approximation (Forrey et al., 2015) which averages the 6D-PES over the "twist" angle between the two molecules. This approximation reduces the rotational coupling while allowing the vibrational motion of both

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molecules to be unrestricted. The calculations are benchmarked against six dimensional close coupling (6D-CC) results which have recently been reported (Yang et al., 2016). Rate coefficients computed with the 6D-CC formulation were found to be in good agreement with 4D-CC calculations (Kalugina et al., 2013) and with the limited experimental data (Brunet et al., 2002) that are available. In general, the CC calculations are computationally inefficient due to the strong rotational coupling. For states with high rotation, the 5D-CS approximation is more efficient than the 4D-CC formulation, which allows many more states to be included in the database. The unrestricted bond distances in the 5D-CS approximation provides better accuracy than the 4D-CS approximation without imposing significant computational costs. Using the 6D-PES, we find good agreement between the CC and CS formulations for most transitions. The resulting database provides a reasonable compromise between accuracy and computational efficiency and yields state-to-state information in a convenient format for use in astrophysical models.

#### 2. Theory

The quantum mechanical CC and CS formulations for diatomdiatom collisions have been given previously (Alexander and DePristo, 1977; Green, 1975; Heil et al., 1978). Here we provide a brief overview of the theory needed to describe the results of the calculations and the notation used in constructing the  $CN + H_2$  database. The potential energy for the four-body system is given by

$$V(\vec{r_1}, \vec{r_2}, \vec{R'}) = U(\vec{r_1}, \vec{r_2}, \vec{R'}) + V(\vec{r_1}) + V(\vec{r_2}),$$
(1)

where  $V(\vec{r_1})$  and  $V(\vec{r_2})$  are the two-body potential energies of the isolated CN and H<sub>2</sub> molecules, and  $U(\vec{r_1}, \vec{r_2}, \vec{R})$  is the four-body interaction potential which vanishes at large separations. The 6D Jacobi coordinate system in Fig. 1 is used where R is the distance between the centers-of-mass of the diatomic molecules,  $\theta_1$  is the angle between  $\vec{r_1}$ and  $\overrightarrow{R}$ ,  $\theta_2$  is the angle between  $\overrightarrow{r_2}$  and  $\overrightarrow{R}$ , and  $\phi$  is the out-of-plane dihedral angle or "twist" angle between the two molecules. The 5D-CS approximation assumes a weak  $\phi$ -dependence and utilizes a suitable average for this degree of freedom (Forrey et al., 2015). It was shown previously (Yang et al., 2016) that the  $\phi$ -dependence for the CN-H<sub>2</sub> PES is relatively weak which justifies the use of this average. Nevertheless, it is necessary to test the approximation against more accurate formulations. Table 1 summarizes the dynamical coordinates, quantum numbers, and constants of motion for each formulation considered in the present work. In all formulations, the interaction potential may be expanded as

$$U(\overrightarrow{r_1}, \overrightarrow{r_2}, \overrightarrow{R}) = \sum_{all \ \lambda} A_{\lambda_1, \lambda_2, \lambda_{12}}(r_1, r_2, R) Y_{\lambda_1, \lambda_2, \lambda_{12}}(\widehat{r_1}, \widehat{r_2}, \widehat{R})$$
(2)

with



**Fig. 1.** Six-dimensional Jacobi coordinates for  $CN + H_2$ . *R* is the distance between the centers of mass of CN and  $H_2$ ,  $r_1$  and  $r_2$  are bond lengths,  $\theta_1$  and  $\theta_2$  are the respective angles between  $\vec{R}$  and  $\vec{r_1}$  and  $\vec{r_2}$ , and  $\phi$  is the dihedral or twist angle. We note that the C and N atoms are reversed compared to the corresponding figure given previously (Yang et al., 2016), which was drawn incorrectly.

#### Table 1

Dynamical formulations, coordinates, and quantum numbers. The spatial inversion parity quantum number may be computed from the quantum numbers listed in the table (Alexander and DePristo, 1977; Green, 1975; Heil et al., 1978).

Formulation	Coordinates	Quantum numbers	Constants
6D-CC 6D-CS 5D-CS 4D-CC <sup>a</sup> 4D-CS <sup>b</sup> 4D-CS <sup>c</sup>	$\begin{array}{c} R, \ r_1, \ r_2, \ \theta_1, \ \theta_2, \ \phi \\ R, \ r_1, \ r_2, \ \theta_1, \ \theta_2, \ \phi \\ R, \ r_1, \ r_2, \ \theta_1, \ \theta_2 \\ R, \ \theta_1, \ \theta_2, \ \phi \\ R, \ \theta_1, \ \theta_2, \ \phi \\ R, \ r_1, \ \theta_1, \ \theta_2, \ \phi \end{array}$	$ \begin{array}{c} v_1, v_2, j_1, j_2, j_{12}, l \\ v_1, v_2, j_1, j_2, j_{12} \\ v_1, v_2, j_1, j_2 \\ j_1, j_2, j_1, j_2 \\ j_1, j_2, j_{12}, l \\ j_1, j_2, j_{12} \\ v_1, j_1, j_2 \end{array} $	J, M l, Ω l, m <sub>1</sub> , m <sub>2</sub> J, M l, Ω l, m <sub>1</sub> , m <sub>2</sub>

<sup>a</sup> Rigid rotor approximation for both molecules. Used in previous work (Kalugina et al., 2013; 2012; Yang et al., 2016) with  $r_1$  fixed at the CN equilibrium distance and  $r_2$  fixed at the average  $H_2(v_2 = 0)$  bond distance.

<sup>b</sup> Rigid rotor approximation for both molecules. Not considered in the present work. <sup>c</sup> Rigid rotor approximation for H<sub>2</sub> and decoupling of the twist-angle. Used in the present work for testing purposes (Figs. 4 and 5) with  $r_2$  fixed at the H<sub>2</sub> equilibrium distance

$$Y_{\lambda_{1},\lambda_{2},\lambda_{12}}(\hat{r}_{1},\,\hat{r}_{2},\,\hat{R}) = \sum_{allm} \langle \lambda_{1}m_{\lambda_{1}}\lambda_{2}m_{\lambda_{2}} | \lambda_{12}m_{\lambda_{12}} \rangle Y_{\lambda_{1}m_{\lambda_{1}}}(\hat{r}_{1}) Y_{\lambda_{2}m_{\lambda_{2}}}(\hat{r}_{2}) Y^{*}_{\lambda_{12}m_{\lambda_{12}}}(\hat{R}),$$
(3)

where  $\langle \dots | \dots \rangle$  represents a Clebsch–Gordan coefficient and  $Y_{\lambda m}(\hat{r})$  is a spherical harmonic. The nuclear wave function for the four-atom system is expanded in terms of a diabatic basis set which contains products of molecular wave functions with vibrational and rotational quantum numbers  $v_i$  and  $j_i$ , respectively. We start by neglecting spin and describe the combined molecular state (CMS) comprised of  $CN(v_1, j_1)$  and  $H_2(v_2, j_2)$  using the notation  $n = (v_1, j_1, v_2, j_2)$ . The potential matrix elements are obtained by integrating over the internal coordinates as described previously (Forrey et al., 2015). Cross sections at a given collision energy  $E_c$  and wavenumber  $k_n$  may be expressed in terms of the appropriate *T*-matrix by

$$\sigma_{n \to n'}^{6D-CC} = \frac{\pi}{k_n^2} [(2j_1 + 1)(2j_2 + 1)]^{-1} \sum_{j_1 \ge j'_1 \ge l'J} (2J + 1) |T_{nj_1 \ge l; n'j'_1 \ge l'}^J|^2$$
(4)

$$\sigma_{n \to n'}^{6D-CS} = \frac{\pi}{k_n^2} [(2j_1 + 1)(2j_2 + 1)]^{-1} \sum_{j_1 j_1' j_1' \bar{l}\Omega} (2\bar{l} + 1) |T_{n;n'}^{\bar{l}\Omega}|^2$$
(5)

$$\sigma_{n \to n'}^{5D-CS} = \frac{\pi}{k_n^2} [(2j_1 + 1)(2j_2 + 1)]^{-1} \sum_{\bar{l}m_1m_2} (2\bar{l} + 1) |T_{n;n'}^{\bar{l}m_1m_2}|^2$$
(6)

for the respective 6D-CC, 6D-CS, and 5D-CS formulations. In Eq. (4), the *T*-matrix is diagonal with respect to the total angular momentum quantum number *J*, defined by the vector relations  $\vec{J} = \vec{l} + \vec{j}_{12}$  and  $\vec{j}_{12} = \vec{j}_1 + \vec{j}_2$ , where *l* is the orbital angular momentum quantum number. In Eq. (5), the *T*-matrix is diagonal with respect to  $\Omega$ , the projection of  $\vec{J}$  on the body-fixed *z*-axis. In Eq. (6), the *T*-matrix is independent of  $\Omega$  and diagonal with respect to  $m_1$  and  $m_2$ , the projection quantum numbers of  $\vec{j}_1$  and  $\vec{j}_2$ . For both CS approximations,  $\vec{l} \equiv J$  is the average value of *l* between  $|J-j_{12}|$  and  $J + j_{12}$ .

For an open shell radical like  $CN(X^2\Sigma^+)$ , it is convenient to use the Hund's case (b) coupling scheme. The CMS for  $CN + H_2$  would then be generalized to  $n = (v_1, N_1, j_1, v_2, j_2)$  where  $\vec{j_1} = \vec{N_1} + \vec{S_1}$  and  $S_1$  is the total electronic spin of CN. The simple cross section formulas (4)-(6) do not apply in this case, however, fine-structure resolved cross sections may be obtained by recoupling the respective spin-independent *T*-matrices (Alexander, 1982; Corey and McCourt, 1983; Offer et al., 1994). For the 5D-CS approximation, the result is

$$\begin{split} \sigma_{n \to n'}^{5D-CS} &= \frac{\pi}{k_n^2} [(2j_1 + 1)(2j_2 + 1)]^{-1} \sum_{\bar{l}m_1m_2\mu_1} (2\bar{l} + 1) T_{n,n'}^{\bar{l}m_1m_2} T_{n,n'}^{*\bar{l}m_1m_2} \\ &\times \begin{pmatrix} S_1 & N_1 & j_1 \\ -m_1' - \mu_1 & m_1' & \mu_1 \end{pmatrix} \begin{pmatrix} S_1 & N_1 & j_1 \\ -m_1 - \mu_1 & m_1 & \mu_1 \end{pmatrix} \\ &\times \begin{pmatrix} S_1 & N_1' & j_1' \\ -m_1' - \mu_1 & m_1' & \mu_1 \end{pmatrix} \begin{pmatrix} S_1 & N_1' & j_1' \\ -m_1 - \mu_1 & m_1 & \mu_1 \end{pmatrix} \end{split}$$
(7)

where  $m_1$  and  $\mu_1$  are the projection quantum numbers of  $N_1$  and  $j_1$ , respectively.

Rate coefficients at a temperature T may be obtained by thermally averaging the cross sections over a Maxwellian velocity distribution

$$q_{n \to n'}(T) = \sqrt{\frac{8k_BT}{\pi\mu}} (k_BT)^{-2} \int_0^\infty \sigma_{n \to n'}(E_c) e^{-E_c/k_BT} E_c \, dE_c \tag{8}$$

where  $\mu$  is the reduced mass of the CN+H<sub>2</sub> system, and  $k_B$  is Boltzmann's constant.

#### 3. Results

All calculations were performed using the 6D PES reported previously (Yang et al., 2016) and accurate diatomic potentials (Feller et al., 2014; Schwenke, 1988). The scattering calculations were performed using a modified version of the TwoBC code (Krems, 2006) which replaces the 6D-CC formulation by the 5D-CS approximation. The radial coordinates of both molecules were represented as discrete variables with 18 points each. Gauss-Legendre quadratures were used for  $\theta_1$  and  $\theta_2$  with 12 points each, and a Chebyshev quadrature with 8 points was used for  $\phi$ . The maximum values for  $\lambda_1$  and  $\lambda_2$  were 8 and 4, respectively. The log-derivative matrix propagation method (Johnson, 1973; Manolopoulos, 1986) was used to integrate the set of coupled equations derived from the Schrödinger equation for R = 5 - 21 a.u. in steps of 0.05 a.u. The parameters given above are identical to those used previously (Yang et al., 2016) which enables a controlled comparison. The calculations were performed in unit steps on a logarithmic energy grid for four sets of collision energies ranging from 1 to 10,000 cm<sup>-1</sup>. The maximum effective orbital angular momentum for each set is given by

$$\bar{L}_{max} = \begin{cases}
20, & E_c = 1 - 10 \text{ cm}^{-1}, \\
40, & E_c = 10 - 100 \text{ cm}^{-1}, \\
80, & E_c = 100 - 1, 000 \text{ cm}^{-1}, \\
160, & E_c = 1, 000 - 10, 000 \text{ cm}^{-1}.
\end{cases}$$
(9)

Excellent agreement was seen at the  $E_c$  boundaries, and extensive convergence tests verified that the results were converged to within 5% or better with respect to the size of the CN rotational basis set for transitions that are not near the truncation limit.

To assess the reliability of the CS calculations, we first benchmark the 5D-CS results against numerically exact 6D-CC results. Fig. 2 shows rotational de-excitation cross sections for CN due to collisions with H<sub>2</sub>. The curves correspond to transitions from the initial states (a) (0, 4, 0, 0) and (b) (0, 4, 0, 1), to the final state indicated in the legend. Solid lines are 5D-CS results and points are 6D-CC results reported previously (Yang et al., 2016). The agreement between the two formulations appears to be acceptable and generally improves with increasing collision energy. Discrepancies occur at small energies where the effective angular momentum  $\overline{l}$  is unable to accurately describe the resonances. Consequently, only a coarse energy grid is used in this region. Other discrepancies occur for energies greater than 1000 cm<sup>-1</sup>, however, here it is likely that the more restricted basis sets for the 6D-CC calculations were not fully converged. Both sets of calculations show significant differences for para-H<sub>2</sub> and ortho-H<sub>2</sub> collisions. For example, the (0, 4,  $(0, 1) \rightarrow (0, 3, 0, 1)$  transition is far more probable at low energies than the  $(0, 4, 0, 0) \rightarrow (0, 3, 0, 0)$  transition. Furthermore, the ortho-H<sub>2</sub> results above ~  $400 \text{ cm}^{-1}$  and all para-H<sub>2</sub> cross sections in Fig. 2 favor an even  $\Delta i_1$  propensity due to the near homonuclear character of CN. This propensity rule is apparently scrambled for ortho-H<sub>2</sub> collisions at lower energies which display a typical exponential energy-gap law behavior. Note, we do not compare these results to earlier works as the 6D-CC results were already shown (Yang et al., 2016) to be in good agreement with 4D-CC rigid-rotor calculations (Kalugina et al., 2013) and to experiment (Brunet et al., 2002).

Fig. 3 shows a similar comparison for (0,11,0,0) and (0,11,0,1) initial states. Here, the solid curves correspond to 5D-CS and the points to 4D-CC results (Yang et al., 2016) using the same PES. The 4D-CC results were previously found to be in good agreement with other calculations (Kalugina et al., 2013) and to experiment (Brunet et al., 2002). The 5D-CS also show good agreement with the 4D-CC results with the exception of the  $\Delta j_1 = -1$  transitions at low energy. Significant differences are again seen between para-H<sub>2</sub> and ortho-H<sub>2</sub> collisions. Similar to Fig. 2,



Fig. 2. State-to-state cross sections for rotational de-excitation of CN due to collision with H<sub>2</sub>. The curves correspond to transitions from the initial states (a) (0, 4, 0, 0) and (b) (0, 4, 0, 1) to the final states indicated in the legend. Solid lines are 5D-CS results and points are 6D-CC results (Yang et al., 2016).



Fig. 3. State-to-state cross sections for rotational de-excitation of CN due to collision with H<sub>2</sub>. The curves correspond to transitions from the initial states (a) (0, 11, 0, 0) and (b) (0, 11, 0, 1) to the final states indicated in the legend. Solid lines are 5D-CS results and points are 4D-CC results (Yang et al., 2016).



Fig. 4. Same as Fig. 2 except that broken curves used basis sets which do not allow rotational excitation of H<sub>2</sub>. The solid and dashed curves correspond to 5D-CS calculations and the dotdashed curves correspond to 4D-CS rigid rotor calculations.

the para-H<sub>2</sub> curves show a strong even  $\Delta j_1$  propensity, whereas the ortho-H<sub>2</sub> curves show larger probabilities for transitions which minimize the internal energy gap.

The basis sets used for all of the results presented in Figs. 2 and 3 included the lowest two rotational levels of para-H<sub>2</sub> or ortho-H<sub>2</sub> symmetry. Similar to previous studies (Kalugina et al., 2013), our data show that rotational transitions for H<sub>2</sub> occur and may be significant. However, due to the low abundance of heavy atoms, astrophysical modeling packages generally do not consider the effect of heavy atom or molecule collisions on H<sub>2</sub> populations. For CN quenching collisions, the H<sub>2</sub> colliders are assumed to not change rotational state, so it is worth investigating the error that is introduced in the calculations when the H<sub>2</sub> basis sets are restricted to their lowest rotational levels. Figs. 4 and 5 show this error for the same initial states considered in Figs. 2 and 3. The solid curves correspond to 5D-CS calculations which used basis sets with  $j_2 = 0$ , 2 for para-H<sub>2</sub> and  $j_2 = 1$ , 3 for ortho-H<sub>2</sub>. The broken curves used the same CN basis sets but restricted H<sub>2</sub> to  $j_2 = 0$  and  $j_2 = 1$  for the two symmetries. The dot-dashed curves correspond to 4D-CS

calculations which further restrict the H<sub>2</sub> bond to its equilibrium position. The plots show that the basis set truncation error is small, and it is less significant than the error introduced by the 4D-CS rigid-rotor approximation. It is interesting that the difference between the 4D-CS and 5D-CS results is larger than the difference between the 4D-CC and 6D-CC results. This suggests that averaging the PES over the twist angle is a better approximation when the radial motion of the internal coordinates is also included. The computational cost of including radial flexibility is modest compared to the cost of rotational coupling. Therefore, we conclude that the 5D-CS approximation with H<sub>2</sub> restricted to the lowest rotational state provides a good compromise between accuracy and efficiency and allows the bulk of the computational effort to be used for handling the large CN rotational basis sets.

Table 2 summarizes rate coefficients for  $CN + H_2$  collisions that have been reported in the literature. We note that the LAMDA file (Schöier et al., 2005) for  $CN + H_2$  was obtained using mass-scaled CN + He data (Lique et al., 2010). The results available on the BASECOL website (Dubernet, 2013) were computed using the 4D-CC formulation



Fig. 5. Same as Fig. 3 except that broken curves used basis sets which do not allow rotational excitation of H<sub>2</sub>. The solid and dashed curves correspond to 5D-CS calculations and the dotdashed curves correspond to 4D-CS rigid rotor calculations.

Table 2Rate coefficients reported for  $CN + H_2$ .

Collider	Transitions	Database	N <sub>1</sub> -range	T-range
para-H <sub>2</sub> ortho-H <sub>2</sub>	fine fine hyperfine rotational rotational fine	present <sup>a</sup> LAMDA <sup>b</sup> BASECOL <sup>c</sup> present <sup>d</sup> BASECOL <sup>e</sup> BASECOL <sup>e</sup>	0-40 0-20 0-12 0-40 0-15 0-12	10–1000 K 5–300 K 5–100 K 10–1000 K 5–300 K 5–100 K

<sup>a</sup> 5D-CS results.

<sup>b</sup> Mass-scaled CN+He results of Lique et al. (2010).

<sup>c</sup> 4D-CC results of Kalugina et al. (2012).

d 6D-CS results.

<sup>e</sup> 4D-CC results of Kalugina et al. (2013).

(rigid-rotor approximation for both molecules) and are expected to be more accurate than the mass-scaled results. For comparisons, it is convenient to obtain rate coefficients by averaging over spin quantum numbers using the formulas

$$q_{N \to N'}(T) = \frac{1}{2} \sum_{j,j'} q_{N,j \to N',j'}(T)$$
(10)

and

$$q_{N,j \to N',j'}(T) = \frac{1}{3} \sum_{F,F'} q_{N,j,F \to N',j',F'}(T)$$
(11)

which are valid for  $j_1 > 1/2$  due to the relations  $\vec{j_1} = \vec{N_1} + \vec{S_1}$  and  $\vec{F_1} = \vec{I_1} + \vec{j_1}$  with  $S_1 = 1/2$  and nuclear spin  $I_1 = 1$  (the subscripts are dropped in the equations for better clarity).

Figs. 6 and 7 show fine-structure resolved rotational quenching rate coefficients for  $\Delta j_1 = \Delta N_1$  and  $\Delta j_1 = \Delta N_1 - 1$  transitions. The present results are compared against data from Kalugina et al. (2012) using the hyperfine average formula (11). The agreement is generally good, particularly for the most efficient transitions. Fig. 6 shows that  $\Delta N_1 = -2$  is the most efficient transition for all initial states. For  $N_1 > 6$ , the  $\Delta N_1 = -4$  transition becomes the second most efficient transition due to the near homonuclear character of CN. The rate coefficients for the  $\Delta j_1 = \Delta N_1 - 1$  rate coefficients shown in Fig. 7. This pattern follows the expected propensity rules (Alexander et al., 1986)

for collisions involving  $^2\Sigma$  molecules.

The agreement between the present results and those of Kalugina et al. (2012) is encouraging considering the different scattering formulation and the different PES used in the two sets of calculations. Furthermore, the agreement appears to improve with increasing temperature. The data from BASECOL stops at T = 100 K and  $N_1 = 12$ . Additional comparisons may be made with the mass-scaled CN+He results available on the LAMDA website. These rate coefficients include fine-structure transitions and may be directly compared to the present calculations. A simpler and more insightful comparison may be made by averaging over the spin states using Eq. (10). This comparison tests the sensitivity of the calculations to the PES and determines whether para-H<sub>2</sub> may be approximated as a closed-shell atom.

Fig. 8 shows rate coefficients for rotational quenching of  $CN(v_1 = 0, j_1 = 20)$  due to para-H<sub>2</sub>. The panels are separated into even and odd rotational changes. The solid curves are 5D-CS results and the dashed curves are the results from LAMDA. The discrepancies with the mass-scaled CN + He results are very large, particularly for the odd  $\Delta j_1$ transitions. The rate coefficients for even  $\Delta j_1$  transitions show some instances of agreement at 10 K, but the mass-scaled CN+He results generally increase more rapidly with T. Qualitatively, it appears that the mass-scaled CN+He results are controlled by dynamical behavior which tends to minimize the internal energy-gap, whereas the dynamical behavior underlying the 5D-CS results tends to produce even  $\Delta j_1$ propensity rules due to the near homonuclear nature of the CN molecule. These results show strong sensitivity to the rotational anisotropy of the PES and demonstrate that attempts to estimate collision data using non-dynamical methods of approximation (e.g. transferring data across collision systems) can lead to very large errors. Dynamical decoupling approximations, while not perfect, generally offer a better means to predict collisional data.

The present database provides  $CN + H_2$  cross sections and rate coefficients for  $j_1 \le 40$ . Because there are no existing data for  $j_1 > 20$  to compare with, we show results for  $j_1 = 30$  and  $j_1 = 40$  together in Fig. 9. The curves follow a similar pattern. For even  $\Delta j_1$  transitions, the  $j_1 = 40$  curves are lower than the  $j_1 = 30$  curves due to the larger energy gaps. The odd  $\Delta j_1$  curves are less predictable and show a stronger temperature dependence for small  $\Delta j_1$  when  $j_1 = 40$ . It should be noted that these results correspond to transitions that are near the truncation edge of the basis set. Therefore, it is expected that these results are less accurate than results for lower rotational levels.

Fig. 10 shows results for ortho-H<sub>2</sub> colliders. BASECOL provides pure



**Fig. 6.** Rate coefficients for  $\Delta j_1 = \Delta N_1$  transitions of CN due to collision with para-H<sub>2</sub>. The initial state corresponds to  $j_1 = N_1 + 0.5$  where  $N_1$  is given in the plots. The present results (solid curves) are compared against BASECOL data from Kalugina et al. (2012) (dashed curves) averaged over hyperfine states.

rotational quenching data (Kalugina et al., 2013) for temperatures up to 300 K, so we neglect fine structure transitions in this comparison. We also consider both the 5D-CS and 6D-CS approximations for ortho- $H_2$  (note: 5D-CS and 6D-CS yield identical results for para- $H_2$  when  $j_2$  is

restricted to be zero). For small values of  $j_1$ , the 5D-CS and 6D-CS results are in reasonably good agreement with each other and with the results from Kalugina et al. (2013). However, the differences between 5D-CS and 6D-CS results appear to become more substantial as  $j_1$  is



Fig. 7. Rate coefficients for  $\Delta j_1 = \Delta N_1 - 1$  transitions of CN due to collision with para-H<sub>2</sub>. The initial state corresponds to  $j_1 = N_1 + 0.5$  where  $N_1$  is given in the plots. The present results (solid curves) are compared against BASECOL data from Kalugina et al. (2012) (dashed curves) averaged over hyperfine states. The same vertical scale is used in Figs. 6 and 7 in order to easily see the propensity for  $\Delta j_1 = \Delta N_1$  transitions.

increased. The largest discrepancies are found for  $\Delta j_1 = -1$  transitions, which is consistent with Fig. 3(b). The 5D-CS calculations were used to obtain fine-structure resolved rotational cross sections and rate

coefficients. The 6D-CS results, however, generally show better agreement with the BASECOL results and are recommended over the 5D-CS data. The recoupling scheme needed to resolve fine-structure



Fig. 8. Rate coefficients for rotational quenching of  $CN(v_1 = 0, j_1 = 20)$  due to collision with para-H<sub>2</sub>. The curves correspond to transitions making (a) even and (b) odd rotational changes. Solid curves are 5D-CS results and dashed curves are mass-scaled results obtained from LAMDA.

transitions was not implemented for the 6D-CS formulation. Therefore, the present database provides fine-structure resolved rotational transitions for the 5D-CS formulation and pure rotational transitions for the 6D-CS formulation.

#### 4. Conclusions

Using an extensive set of 5D-CS calculations, we constructed a database of cross sections and rate coefficients for  $CN + H_2$  collisions. The database includes fine-structure resolved rotational transitions for initial  $CN(v_1 = 0, j_1 = 0 - 40)$  with  $H_2$  constrained to the lowest rovibrational level for the given symmetry. Vibrational coupling was found to be negligible for rotational transitions within  $v_1 = 0$ . The molecular bonds are not assumed to be rigid, however, which allows variation in the PES to be taken into account as the molecules vibrate. This was shown to provide better agreement with the results of the 6D-CC formulation compared to 4D-CS calculations which restrict the bonds to their equilibrium positions. We note that rotational transitions for  $H_2$ occur and may be important. However, astrophysical modeling codes generally neglect the effect of heavy molecule collisions on  $H_2$  populations. Therefore, we have truncated the  $H_2$  basis sets in order to allow the bulk of the computational effort to be used for handling the large CN rotational basis sets. The error introduced by this truncation was shown to be small for the (0,4,0,0), (0,4,0,1), (0,11,0,0), and (0,11,0,1) initial states. The database for ortho- $H_2$  collisions also includes 6D-CS calculations for pure rotational transitions.

Cross sections are given over the energy range  $1-10,000 \text{ cm}^{-1}$  and rate coefficients over the temperature range 10-1,000 K. Additional details are provided in the supplementary material associated with this article. The database may be downloaded from the UGA Excitation Database (UGA, http://www.physast.uga.edu/amdbs/excitation/) or PSU website (PSU, http://www.physics.bk.psu.edu/sigma/index.html). The present set of calculations does not include hyperfine structure which may be important in detailed astrophysical modeling. Nevertheless, its neglect is expected to be less significant than the error introduced through the use of mass-scaled CN+He data. Generally good agreement is found for rate coefficients in the present database and those obtained from the BASECOL website. The extended



**Fig. 9.** Rate coefficients for rotational quenching of  $CN(v_1 = 0, j_1 = 30)$  and  $CN(v_1 = 0, j_1 = 40)$  due to collision with para-H<sub>2</sub>. The results are presented for (a) even and (b) odd rotational changes with solid curves for  $j_1 = 30$  and dashed curves for  $j_1 = 40$ .



Fig. 10. Rate coefficients for rotational quenching of CN due to collision with ortho-H<sub>2</sub>. The solid curves (5D-CS) and dashed curves (6D-CS) are compared against BASECOL data from Kalugina et al. (2013) (points).

temperature range and increased number of rotational levels provided by the present database, and inclusion of vibrational transitions in future versions of the database, should enable more reliable modeling of molecular clouds and young stellar objects.

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#### Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molap.2018.03.001.

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- Molecular Astrophysics 11 (2018) 23-32
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