

Hyperfine excitation of CN by para- and ortho-H₂

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Accepted 2014 September 22. Received 2014 September 22; in original form 2014 September 8

ABSTRACT

Among the interstellar molecules, the CN radical is of particular interest since it is a good probe of cold dark molecular clouds, and especially prestellar cores. Modelling of CN emission spectra from these dense molecular clouds requires the calculation of rate coefficients for excitation by collisions with the most abundant species. We calculate fine- and hyperfine-structure-resolved excitation rate coefficients of CN($X^2\Sigma^+$) by para- and ortho-H₂. The calculations are based on a new potential energy surface obtained recently from highly correlated ab initio calculations. State-to-state rate coefficients between fine and hyperfine levels of CN were calculated for low temperatures ranging from 5 to 100 K. The new results are compared to available CN rate coefficients. Significant differences are found between the different sets of rate coefficients. This comparison shows that the new CN–H₂ rate coefficients have to be used for observations interpretations. We expect that their use will help significantly to have a new insight into the physical conditions of prestellar cores.

Key words: molecular data – molecular processes – ISM: molecules.

1 INTRODUCTION

Observations of cyano radical (CN) have been assumed to be of particular importance in the context of low-mass star formation, as it is present in the prestellar cores, even at the low temperatures (of the order of 10 K) which characterize these molecular clouds (Keto & Caselli 2008). Indeed, dense cores, and especially prestellar cores, suffer from strong depletion of most molecular tracers (CS, CO, . . . ; Pagani et al. 2005). Only a few species survive in the gas phase and among them, nitrogen-carrying molecules such as CN, HCN or HNC are the best known (Hily-Blant et al. 2008, 2010).

In order to accurately interpret CN observations and, hence, be able to determine physical conditions in prestellar cores, hyperfine-resolved rate coefficients of CN by its principal interstellar collisional partner, H₂, are required. Without these rates, only approximate estimates of physical conditions are possible assuming local thermodynamic equilibrium, which at the typical densities of dense interstellar clouds is generally not a good approximation (Lique et al. 2009; van der Tak 2011).

The first realistic CN rate coefficients were provided only recently. CN–He data (as a model for CN–H₂) taking into account the fine and hyperfine structure of CN were provided by Lique et al. (2010) and Lique & Klos (2011), respectively. Preliminary calculations for fine and hyperfine excitation of CN by H₂($j = 0$) were also provided recently by some of us (Kalugina, Lique & Klos 2012). However, in this study, the rotational structure of H₂ was ignored,

whereas it is well known that, generally, collisions with para- and ortho-H₂ differ significantly (Roueff & Lique 2013). In addition, CN–para-H₂($j = 0$) data could be uncertain because of the lack of inclusion of H₂ structure in the scattering calculations.

Taking into account the importance of having accurate CN–H₂ rate coefficients, it is crucial to extend the latter calculations in order to provide H₂ rotationally dependent data. The determination of fine-structure-resolved rate coefficients for collisions of open shell molecules with para- and ortho-H₂ is a real challenge from the theoretical point of view that has been overcome by some of us (Kalugina, Klos & Lique 2013). In this Letter, we aim to incorporate the hyperfine structure of the CN molecule in the rate coefficient calculations.

This Letter is organized as follows. Section 2 describes the ab initio potential energy surface (PES) used in this work and provides a brief description of the theory and the calculations. In Section 3, we present and discuss our results. Conclusions of this work are drawn in Section 4.

2 METHODOLOGY

2.1 Potential energy surface

In this Letter, we used the recently published PES calculated by some of us (Kalugina et al. 2013, hereafter Paper I). Calculations of the CN($X^2\Sigma^+$)–H₂ PES are described in detail in Paper I. We only present here a short description of the PES.

Ab initio calculations of the PES of CN–H₂ van der Waals complex were carried out at the coupled cluster with single, double

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and perturbative triple excitations (CCSD(T); Knowles, Hampel & Werner 1993, 2000) level of theory using the MOLPRO 2010 package (Werner et al. 2010). The four atoms were described by the aug-cc-pVTZ basis set of Woon & Dunning (1994) augmented by the (3s, 2p, 1d) bond functions, as defined by Williams et al. (1995).

In order to solve the close-coupling scattering equations, we expanded the PES over angular functions using the expression of Green (1975). The angular functions are formed from coupled spherical functions $Y_{l_i m_i}(\alpha, \beta)$ which are associated with the rotational angular momenta of CN and H₂.

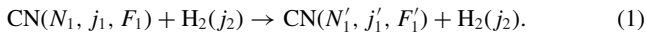
The global minimum of the PES occurs for C-N . . . H-H collinear geometry ($\theta = \theta' = \phi = 0^\circ$) at $R = 7.23 a_0$. The well depth is 121.36 cm^{-1} . The experimental dissociation energy of the CN-ortho-H₂ complex ($D_0 = 38 \pm 2 \text{ cm}^{-1}$; Chen & Heaven 1998) was well reproduced by the calculated value from our PES ($D_0 = 38.75 \text{ cm}^{-1}$; Paper I). Such agreement shows the accuracy of the PES.

Rate coefficients obtained from this PES were found to be in good agreement with the experimental rotational (with unresolved fine- and hyperfine-structure) rate coefficients of Brunet et al. (2002, see Paper I).

2.2 Scattering calculations

The CN($^2\Sigma^+$) fine-structure levels are labelled by N_1, j_1 , where N_1 is the rotational angular momentum and j_1 the total molecular angular momentum quantum number with $\mathbf{j}_1 = \mathbf{N}_1 + \mathbf{S}_1$, where S_1 is the electronic spin. Two kinds of levels exist, the levels with $j_1 = N_1 + 1/2$ and those with $j_1 = N_1 - 1/2$. The nitrogen atom also possesses a non-zero nuclear spin ($I_1 = 1$). The coupling between I_1 and \mathbf{j}_1 results in a weak splitting of each level into three hyperfine levels (except for the $j_1 = 1/2$ level which is split into only two levels). Each hyperfine level is designated by a quantum number F_1 ($\mathbf{F}_1 = \mathbf{I}_1 + \mathbf{j}_1$) varying between $|I_1 - j_1|$ and $I_1 + j_1$. The H₂ rotational levels are designated by j_2 .

In this Letter, we focus on the following process:



We only consider the transitions where j_2 remains fixed, and equal to 0 (para-H₂) and 1 (ortho-H₂). However, the scattering calculations include the possibility of H₂ rotational excitation during the collision even if their probability is very low.

Recent scattering calculations considering the fine-structure excitation of CN by para- and ortho-H₂ have been published in Paper I. We refer the reader to Paper I for details. In summary, electronic spin-free scattering calculations were performed with the MOLSCAT program (Hutson & Green 1994) using a close-coupling approach (Green 1975). Calculations were carried out for energies up to 1200 cm^{-1} . Collisions of CN with both para-H₂ and ortho-H₂ were considered. Fine-structure-resolved S-matrices and cross-sections were obtained using a recoupling technique (Alexander & Dagdigan 1985). The validity of the recoupling approach was checked. The accuracy was better than 1 per cent compared to a full close-coupling approach (Paper I).

In this Letter, we extend the calculation of Paper I to the hyperfine structure. Hyperfine-resolved rate coefficients could be obtained directly from fine-structure-resolved rate coefficients using infinite-order sudden methods (Faure et al. 2012; Lanza & Lique 2014). However, Lanza & Lique (2014) found that such an approach was not accurate for low temperatures and for collisions with ortho-H₂.

Then, we use the following methodology in order to obtain accurate hyperfine-resolved rate coefficients. The hyperfine splitting of

the CN energy levels is very small. Hence, hyperfine levels are assumed to be degenerate, so that the hyperfine scattering problem can be simplified considerably. The integral cross-sections corresponding to transitions between hyperfine levels of the CN molecule are then obtained from nuclear spin-free S-matrices using a recoupling method, as we did in Paper I for the fine structure. The recoupling scheme of the angular momenta is adopted to transform S-matrices to a new recoupled basis (Offer, van Hemert & van Dishoeck 1994).

First, we couple the rotational angular momenta of the two diatomic molecules to form $\mathbf{j}_{12} = \mathbf{j}_1 + \mathbf{j}_2$, which then couples with the relative angular momentum of these molecules, l , to form the total angular momentum $\mathbf{J} = \mathbf{j}_{12} + \mathbf{l}$ (without nuclear spin of the target). The total angular momentum of a system including nuclear spin is, then, given by

$$\mathbf{J}_T = \mathbf{J} + \mathbf{I}_1. \quad (2)$$

In the recoupling scheme, we introduce a new perturbing angular momentum \mathbf{j}_R , and recouple the angular momenta as follows:

$$\mathbf{j}_R = \mathbf{j}_2 + \mathbf{l}, \quad \mathbf{J}_T = \mathbf{j}_R + \mathbf{F}_1. \quad (3)$$

Transformation to the new basis leads to the recoupling of S-matrices obtained from nuclear spin-free (but fine-structure-resolved) calculations (Offer et al. 1994; Paper I):

$$\begin{aligned} & S^{J_T} (N_1 j_1 j_2 l j_R F_1 | N'_1 j'_1 j'_2 l' j'_R F'_1) \\ &= \sum_{J, j_{12}, j'_{12}} (-1)^{j_R + j'_R + l + l' + j_2 + j'_2} S^J (N_1 j_1 j_2 j_{12} l | N'_1 j'_1 j'_2 j'_{12} l') \\ &\quad \times [(2F_1 + 1)(2F'_1 + 1)(2j_{12} + 1) \\ &\quad \times (2j'_{12} + 1)(2j_R + 1)(2j'_R + 1)]^{1/2} (2J + 1) \\ &\quad \times \begin{Bmatrix} j_1 & j_2 & j_{12} \\ l & J & j_R \end{Bmatrix} \begin{Bmatrix} j'_1 & j'_2 & j'_{12} \\ l' & J & j'_R \end{Bmatrix} \\ &\quad \times \begin{Bmatrix} j_R & j_1 & J \\ I_1 & J_T & F_1 \end{Bmatrix} \begin{Bmatrix} j'_R & j'_1 & J \\ I_1 & J_T & F'_1 \end{Bmatrix}, \quad (4) \end{aligned}$$

where $\begin{Bmatrix} \end{Bmatrix}$ is the ‘6- j ’ symbol and where $S^J(N_1 j_1 j_2 j_{12} l | N'_1 j'_1 j'_2 j'_{12} l')$ are the S-matrices obtained from nuclear spin-free calculations.

Thus, the hyperfine-structure-resolved cross-sections are then given by

$$\begin{aligned} \sigma_{N_1, j_1, F_1, j_2 \rightarrow N'_1, j'_1, F'_1, j'_2} &= \frac{\pi}{k_{N_1, j_1, j_2}^2 (2F_1 + 1)(2j_2 + 1)} \\ &\times \sum_{J_T} (2J_T + 1) \sum_{l, l', j_R, j'_R} |T^{J_T} (N_1 j_1 j_2 l j_R F_1 | N'_1 j'_1 j'_2 l' j'_R F'_1)|^2, \quad (5) \end{aligned}$$

where $T = 1 - S$ and $k_{N_1, j_1, j_2}^2 = 2\mu(E - E_{N_1, j_1} - E_{j_2})$.

μ is the reduced mass of the system, E is the total energy of the system, and E_{N_1, j_1} and E_{j_2} are the internal energy of CN and H₂ respectively.

From the rotationally inelastic cross-sections $\sigma_{N_1, j_1, F_1, j_2 \rightarrow N'_1, j'_1, F'_1, j'_2}(E_c)$, one can obtain the corresponding thermal rate coefficients at temperature T by an average over the collision energy (E_c):

$$\begin{aligned} k_{N_1, j_1, F_1, j_2 \rightarrow N'_1, j'_1, F'_1, j'_2}(T) &= \left(\frac{8}{\pi \mu k_B^3 T^3} \right)^{1/2} \\ &\times \int_0^\infty \sigma_{N_1, j_1, F_1, j_2 \rightarrow N'_1, j'_1, F'_1, j'_2}(E_c) e^{-\frac{E_c}{k_B T}} dE_c, \quad (6) \end{aligned}$$

where k_B is Boltzmann's constant and μ is the reduced mass of the CN–H₂ complex.

3 RESULTS

3.1 CN–H₂ rate coefficients

Using the computational scheme described above, we have obtained inelastic (fine and hyperfine) cross-sections up to the total energy of 1200 cm⁻¹ for transitions between the first 76 hyperfine levels of CN ($N_1, N'_1 \leq 12$). Calculations up to the total energy of 1200 cm⁻¹ allow us to determine the corresponding rate coefficients up to 100 K. The complete set of (de-)excitation rate coefficients will be made available through the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) databases.

Figs 1 and 2 present the temperature variation of CN–para-H₂ and CN–ortho-H₂ rate coefficients, respectively, for selected $N_1 = 2, j_1, F_1 \rightarrow N'_1 = 1, j'_1, F'_1$ transitions.

First of all, there is significant differences between the collisions with the two H₂ species, the cross-sections with H₂($j_2 = 1$) being significantly larger than the ones with H₂($j_2 = 0$) for odd ΔN_1

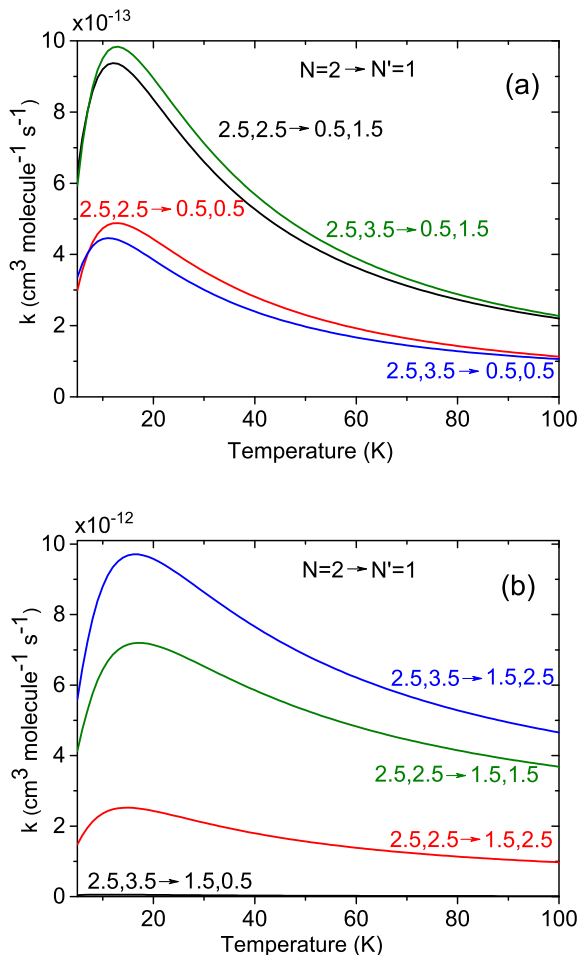


Figure 1. Temperature variation of the hyperfine-resolved CN–para-H₂ rate coefficients for $N_1 = 2, j_1, F_1 \rightarrow N'_1 = 1, j'_1, F'_1$ transitions. Panel (a) corresponds to $\Delta j_1 \neq \Delta N_1$ transitions. Panel (b) corresponds to $\Delta j_1 = \Delta N_1$ transitions.

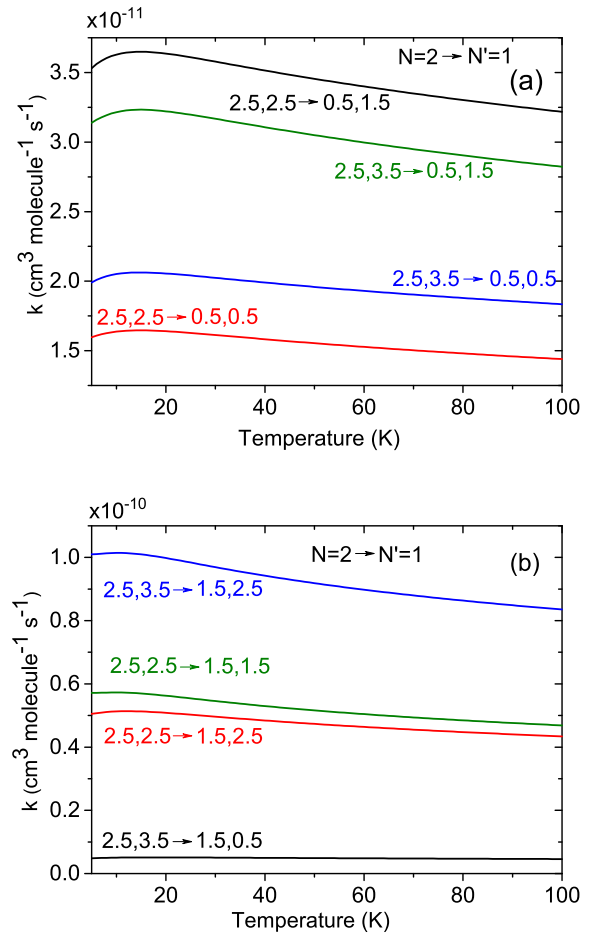


Figure 2. Temperature variation of the hyperfine-resolved CN–ortho-H₂ rate coefficients for $N_1 = 2, j_1, F_1 \rightarrow N'_1 = 1, j'_1, F'_1$ transitions. Panel (a) corresponds to $\Delta j_1 \neq \Delta N_1$ transitions. Panel (b) corresponds to $\Delta j_1 = \Delta N_1$ transitions.

transitions as already found in Paper I. Significant anisotropy of the PES obtained from different H₂ orientations explains this behaviour.

Then, we can also observe a strong propensity rule in favour of $\Delta N_1 = \Delta j_1$ transitions for both para- and ortho-H₂ collisions. This behaviour, predicted theoretically (Alexander, Smedley & Corey 1986), is a general feature of collisions of molecules in $2^5 + 1 \Sigma$ electronic state, as shown previously for the O₂–H₂ (Lique et al. 2014) or SO–H₂ (Lique et al. 2007) collisions.

Finally, for $\Delta j_1 = \Delta N_1$ transitions, we have a strong propensity rule in favour of $\Delta j_1 = \Delta F_1$ hyperfine transitions for both para- and ortho-H₂ collisions. This trend is the usual trend for open-shell molecules (Alexander 1985). For $\Delta j_1 \neq \Delta N_1$ transitions, no clear hyperfine propensity rules can be extracted.

3.2 Comparison with previous results

It is interesting to compare the present rate coefficients with those of Lique & Klos (2011, hereafter LK11) calculated for CN–He collisions. Collisions with He are often assumed to model collisions with para-H₂($j_2 = 0$), and it is generally assumed that rate coefficients with para-H₂($j_2 = 0$) should be larger than rate coefficients with He owing to the smaller reduced mass of the collisional system, the scaling factor being 1.36 (Schöier et al. 2005).

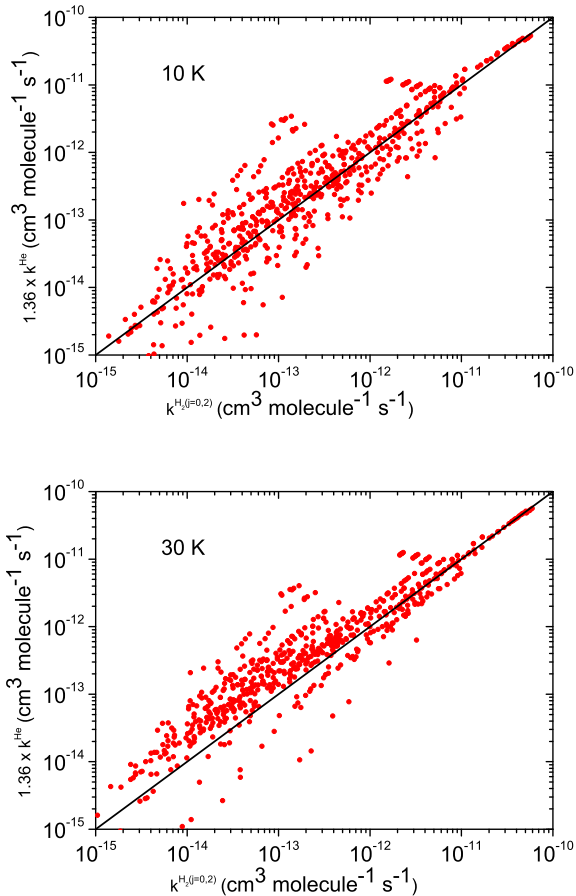


Figure 3. Comparison between present CN–H₂ hyperfine rate coefficients and the CN–He ones of LK11. De-excitation rate coefficients are reported at 10 and 30 K. The horizontal axis represents the present CN–H₂ rate coefficients and the vertical axis represents the corresponding CN–He ones.

Fig. 3 presents, at 10 and 30 K, a systematic comparison between present hyperfine CN–para-H₂ rate coefficients and the CN–He ones of LK11, multiplied by a factor of 1.36.

As one can see, the scaling factor is clearly different from 1.36. The difference can be up to an order of magnitude. Such differences are simply explained by the different collisional partners (He versus H₂). The low collisional energies cross-sections are very sensitive to the shape and depth of the PES well and it is not surprising to see significant differences between the two collisional systems at low temperatures.

We also compare our new CN–para-H₂ results with those of Kalugina et al. (2012, hereafter KLK12). KLK12 computed hyperfine-resolved CN–H₂($j = 0$) neglecting the rotational structure of H₂ and using a PES averaged over H₂ rotation. The accuracy of such approximation is difficult to estimate and the present comparison will help in this goal. Fig. 4 presents, at 10 and 100 K, a systematic comparison between present hyperfine CN–para-H₂ rate coefficients and the CN–para-H₂ ones of KLK12.

The overall agreement between the two sets of data is good for all the temperature range considered in this work. The inclusion of H₂($j_2 = 2$) in the H₂ rotational basis moderately impacts the magnitude of the rate coefficients (particularly those with the highest magnitude) so that old and new results diverge by less than a factor of 2.

Contrary to the rate coefficients with a low magnitude, the agreement between the two sets of data increases with increas-

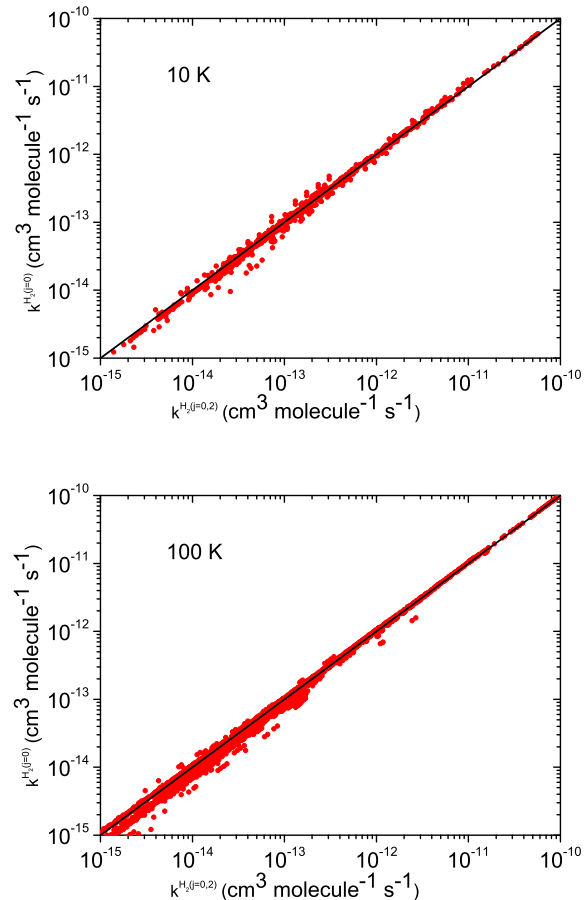


Figure 4. Comparison between present CN–H₂ hyperfine rate coefficients and the CN–H₂ ones of KLK12. De-excitation rate coefficients are reported at 10 and 100 K. The horizontal axis represents the present CN–H₂ rate coefficients and the vertical axis represents the corresponding CN–He ones.

ing temperature for the rate coefficients with high magnitude ($k > 10^{-12}$ cm³ mol⁻¹ s⁻¹). Such behaviour could have been anticipated. Indeed, excitation cross-sections sensitivity with respect to the PES decreases with increasing energies. To conclude, a reasonable description (within a factor of 2) of the scattering of CN with para-H₂($j_2 = 0$), the main collisional partner in cold molecular clouds, can be obtained by the simplified treatment in which we use only the CN–H₂($j_2 = 0$) PES.

Then, it can be asked if such differences can imply significant consequences on the astrophysical modelling. Several studies (e.g. review of Roueff & Lique 2013) were devoted to the sensitivity of radiative transfer calculations to rate coefficients. It was generally found that an accuracy of 20–30 per cent is enough but that a factor of 2 may lead to uncertainties in the astrophysical modelling. This is why we recommend the use of our new CN–H₂ data for astrophysical modelling, particularly if ortho-H₂ abundance is not negligible.

4 CONCLUSION

We have used quantum scattering calculations to investigate rotational energy transfer in collisions of CN($X^2\Sigma^+$) with both para- and ortho-H₂ molecules. The calculations are based on a new, highly correlated PES. Fine- and hyperfine-state-resolved rate coefficients were determined for temperatures ranging from 5 to 100 K. The

collisional data with the ortho-H₂ colliding partner are the first one for the CN molecule. These CN–H₂ rate coefficients, along with the OH–H₂ data from Offer et al. (1994), are the only available data that consider both the fine and the hyperfine structure of the target in the case of collisions with ortho-H₂.

The propensity rules were studied and the only well-defined propensity rule is in favour of $\Delta j_1 = \Delta N_1 = \Delta F_1$ transitions. It is important to specify that the hyperfine rate coefficients computed in this Letter are not independent of the initial hyperfine level and not proportional to the degeneracy ($2F_1' + 1$) of the final hyperfine level so that the hyperfine structure have to be considered through accurate quantum mechanical calculations.

Finally, the comparison of the new CN–H₂ rate coefficients with the existing CN–He and CN–H₂ ones shows that differences exist between the different sets of data. Hence, the present CN–H₂ rate coefficients have to be used for observations' interpretations and we expect that their use will help significantly in the interpretation of the CN emission lines observed with current and future telescopes. Nevertheless, it has been found that a reasonable description (within a factor of 2) of the scattering between CN and para-H₂ ($j_2 = 0$) can be obtained using a simplified approach that neglects the rotation of the H₂ molecule. As a consequence, ¹³CN–H₂ ($j_2 = 0$) or C¹⁵N–H₂ ($j_2 = 0$) rate coefficients that are also crucially needed for modelling of prestellar cores may be rapidly calculated using this reasonable theoretical approach.

ACKNOWLEDGEMENTS

We thank J. Klos for helpful discussions. This work has been supported by the Agence Nationale de la Recherche (ANR-HYDRIDES), contract ANR-12-BS05-0011-01 and by the CNRS national programme 'Physique et Chimie du Milieu Interstellaire'. We also thank the CPER Haute-Normandie/CNRT/Energie, Electronique, Matériaux. The dynamical calculations were performed using HPC resources of SKIF-Cyberia (Tomsk State University).

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