

CN excitation in cold molecular clouds and in circumstellar envelope

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INTRODUCTION

- CN molecule is one of the most widely distributed in ISM.
- The CN thermal lines probe dense regions in molecular clouds and circumstellar envelopes.
- Modelling of molecular emission spectra from ISM requires the knowledge of accurate rate coefficients for excitation by collisions with the most abundant species. Without these rates, only approximate estimates of the molecular abundance are possible.

At low temperatures, collisional energy transfer affects the population of rotational levels of CN. We present state-to-state rate coefficients between the first 25 fine and 76 hyperfine levels of CN($X^2\Sigma^+$), being in the ground vibrational state, in collisions with $H_2(j=0)$. The new fine and hyperfine-structure resolved rate coefficients are the first ones obtained for the CN radical in collision with H_2 .

In circumstellar envelope, CN radical can be produced by photodissociation of HCN. The products could be both in the ground and excited vibrational states. However, CN is observed only in its ground vibrational state. Thus, it is crucial to study the vibrational de-excitation of CN by the most abundant collisional partners. We present the study of vibrational relaxation of CN($v=1$) by He. Modeling of the chemistry of circumstellar envelope performed in the laboratory of Rennes included CN+hydrocarbons reactions done in Ar bath. Thus, in order to interpret the experiments, we have also studied vibrational relaxation of CN($v=1$) by Ar.

METHODS

Ab initio calculations

CN- H_2

$\langle r^{HH} \rangle_0 = 1.4487 a_0$
 $r_e^{CN} = 2.2144 a_0$

Interaction potential was calculated at the RCCSD(T) level using aVTZ basis set plus (3s, 2p, 1d) bond functions (using MOLPRO package [1]).

Interaction potential is expanded in spherical functions:

$$V(R, \theta, \theta', \phi) = \sum_{l,l',\mu} v_{l,l',\mu}(R) s_{l,l',\mu}(\theta, \theta', \phi)$$

$$s_{l,l',\mu}(\theta, \theta', \phi) = \left(\frac{2l+1}{4\pi}\right)^{1/2} \left\{ \sum_m (-1)^m (2 - \delta_{m0}) \langle lm'l-m | ll'\mu 0 \rangle P_{lm}(\theta) P_{l'm}(\theta') \cos(m\phi) \right\}$$

Here l, l' are associated respectively with the rotational motion of CN and H_2 . The homonuclear symmetry of H_2 forces the index l' to be even.

CN-He/Ar

Interaction energy was calculated at the SAPT(DFT) level with PBE0 functional in aVTZ basis set plus (3s 3p 2d 2f) bond functions using SAPT2008 package [2] (SAPT.os for open shell systems).

Interaction potential is expanded as follows:

$$V(r, R, \theta) = \sum_{n=1}^{N_{max}} \sum_{l=1}^{L_{max}} d_{m,0}^{l+m-1}(\cos \theta) A_{ln}(R) (r - r_e)^{n-1}$$

$d_{m,0}^{l+m-1}(\cos \theta)$ - reduced Wigner rotation matrix elements,
 N_{max} - number of bond distances

Scattering calculations

CN- H_2

At low temperatures ($T \leq 100$ K), the rotational excitation probability of H_2 is low, the energy spacing between the $j=0$ and $j=2$ levels in para- H_2 being 510 K. Hence, we restrict H_2 to its lowest rotational level: $j=0$.

4D PES \rightarrow 2D PES $V_{av}(R, \theta) = \sum_l V_l(R) P_l(\cos \theta)$

where $V_{av}(R, \theta)$ is obtained by an average of $V(R, \theta, \theta', \phi)$ over the angular motion $\{\theta', \phi\}$ of the H_2 molecule.

The hyperfine structure levels are labeled by N, j, F .

$$\vec{j} = \vec{N} + \vec{S} \quad \vec{F} = \vec{I} + \vec{j}$$

N is the rotational angular momentum and j the total molecular angular momentum quantum number, I - nuclear spin.

We used Alexander's description [3] of the inelastic scattering and a quantum close-coupling calculations to obtain $S^J(j; j')$ scattering matrix and integral cross sections corresponding to $N_j \rightarrow N_{j'}$ transition between fine structure levels of CN. J and l denote the total angular momentum ($J = j + l$) and the orbital angular momentum quantum numbers.

The integral hyperfine cross sections can be obtained from scattering S-matrix between fine structure levels using the recoupling method [4]:

$$\sigma_{N_j F \rightarrow N_{j'} F'} = \frac{\pi}{k_{N_j F}^2} (2F' + 1) \sum_K \left\{ \begin{matrix} j & j' & K \\ F & F' & I \end{matrix} \right\}^2 P^K(j \rightarrow j')$$

Tensor opacities $P^K(j \rightarrow j') = \frac{1}{2K+1} \sum_l |T^K(j; j')|^2$

Thermal rate coefficients at temperature T (average over the collision energy) [5]:

$$k_{N_j F \rightarrow N_{j'} F'}(T) = \left(\frac{8}{\pi \mu k_B^3 T^3}\right)^{1/2} \int_0^\infty \sigma_{N_j F \rightarrow N_{j'} F'} E_c e^{-E_c/k_B T} dE_c$$

Total energy grid: 0.2 - 1000 $cm^{-1} \rightarrow$ rate coefficients for up to 100 K.
 The integration range was set from 4.5 a_0 to 80 a_0 .
 Scattering calculations were carried out using HIBRIDON [6]

Scattering calculations

CN-He/Ar

We used vibrational Close-Coupling rotational Infinite Order Sudden method [7] (the rotational levels are treated as being degenerate) for scattering calculations. The S-matrix elements must be multiplied by the appropriate spherical harmonics and integrated over θ to give the fundamental IOS cross sections

$$\sigma^{IOS}(v, 0 \rightarrow v', L)(E)$$

The de-excitation ro-vibrational cross sections are written as [7]:

$$\sigma^{IOS}(v, j \rightarrow v', j') = \sum_L (2j'+1) \begin{pmatrix} j' & j & L \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma^{IOS}(v, 0 \rightarrow v', L)$$

Calculation were carried out using MOLSCAT [8] package.

To ensure the convergence of cross sections out of $v=1$ we have included vibrational level $v=2$ (convergence to less than 1%). The vibrational relaxation cross sections were obtained as follows:

$$\sigma(v \rightarrow v') = \sum_{j'} \sigma^{IOS}(v, j=0 \rightarrow v', j')$$

Rate coefficients are obtained by overaging appropriate cross sections over a Boltzman distribution of velocities at a given kinetic temperature T :

$$k_{v \rightarrow v'} = \left(\frac{8\beta^3}{\pi \mu}\right)^{1/2} \int_0^\infty \sigma(v \rightarrow v')(E_k) \times E_k \exp(-\beta E_k) dE_k$$

$$\beta = (k_B T)^{-1} \quad E = E_k + \epsilon_v$$

E - total energy, E_k - kinetic energy, ϵ_v - energy of vibrational level

Total energies: up to 15 000 $cm^{-1} \rightarrow$ converged rate coefficients up to 1500 K.

RESULTS

Fine Structure excitation

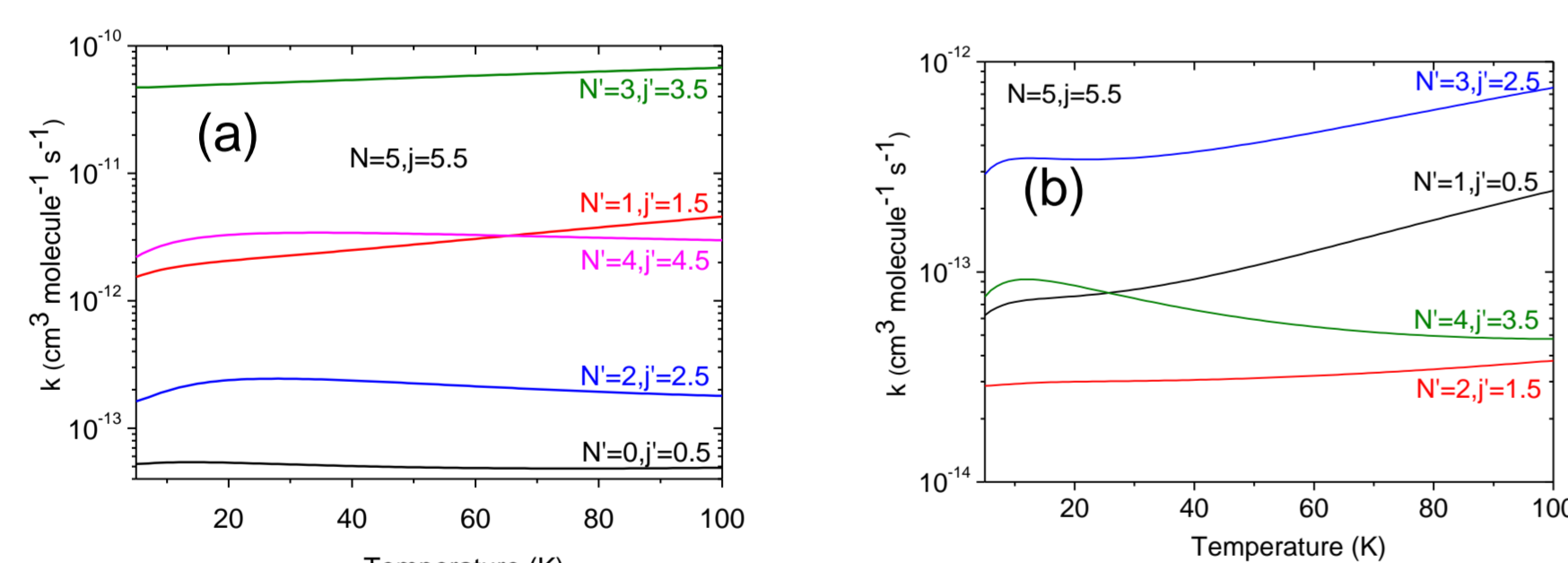


Fig. 1 Temperature dependence of CN- $H_2(j=0)$ rate coefficients for $\Delta j = \Delta N$ (a) and $\Delta j \neq \Delta N$ (b) transitions out of $N, j = 5, 5.5$.

- Strong propensity rule for $\Delta j = \Delta N$ transitions (predicted theoretically [9] for collisions of molecules in $2S+1\Sigma$ electronic state).
- Strong propensity for transitions with even ΔN .

Near-homonuclear symmetry of the PES strongly favors transitions with even ΔN (as in Ref. [10], for example).

Hyperfine Structure excitation

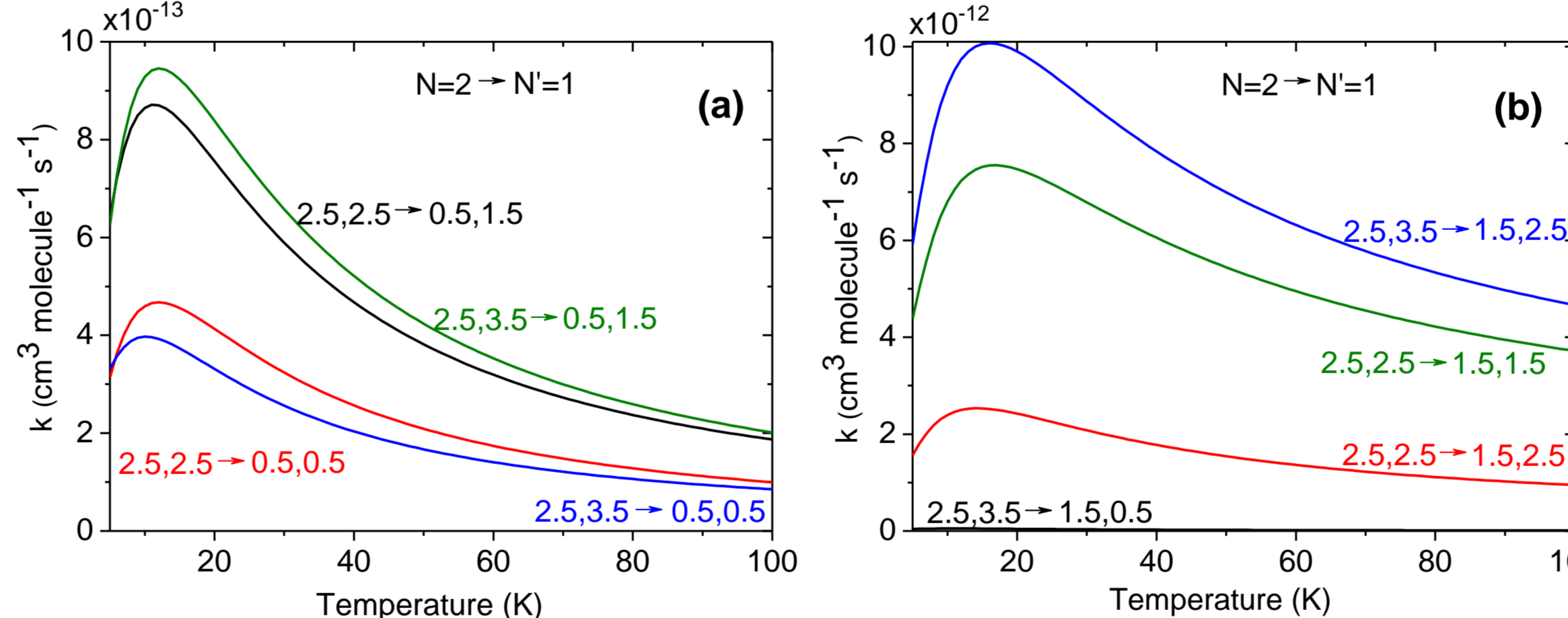


Fig. 2 Temperature variation of the hyperfine-resolved CN- H_2 rate coefficients for $N=2, j, F \rightarrow N'=1, j', F'$ transitions. Panel (a) corresponds to $\Delta j = \Delta N$ transitions. Panel (b) corresponds to $\Delta j \neq \Delta N$ transitions.

$\Delta j = \Delta N$ transitions (Fig. 2a): strong propensity rule in favor of $\Delta j = \Delta F$ transitions, especially when N increases. This trend is usual for open-shell molecules (for instance, CN-He collisions [11]).

$\Delta j \neq \Delta N$ transitions (Fig. 2b): no clear propensity rules can be extracted. Two rules:
 •rate coefficients show propensity in favor of $\Delta j = \Delta F$ transitions
 •final distribution seems to be proportional to the degeneracy $(2F' + 1)$ of the final hyperfine level

The complete set of de-excitation rate coefficients with $N, N' \leq 12$ is available online at the LAMBDA [12] website.

CN-He/Ar

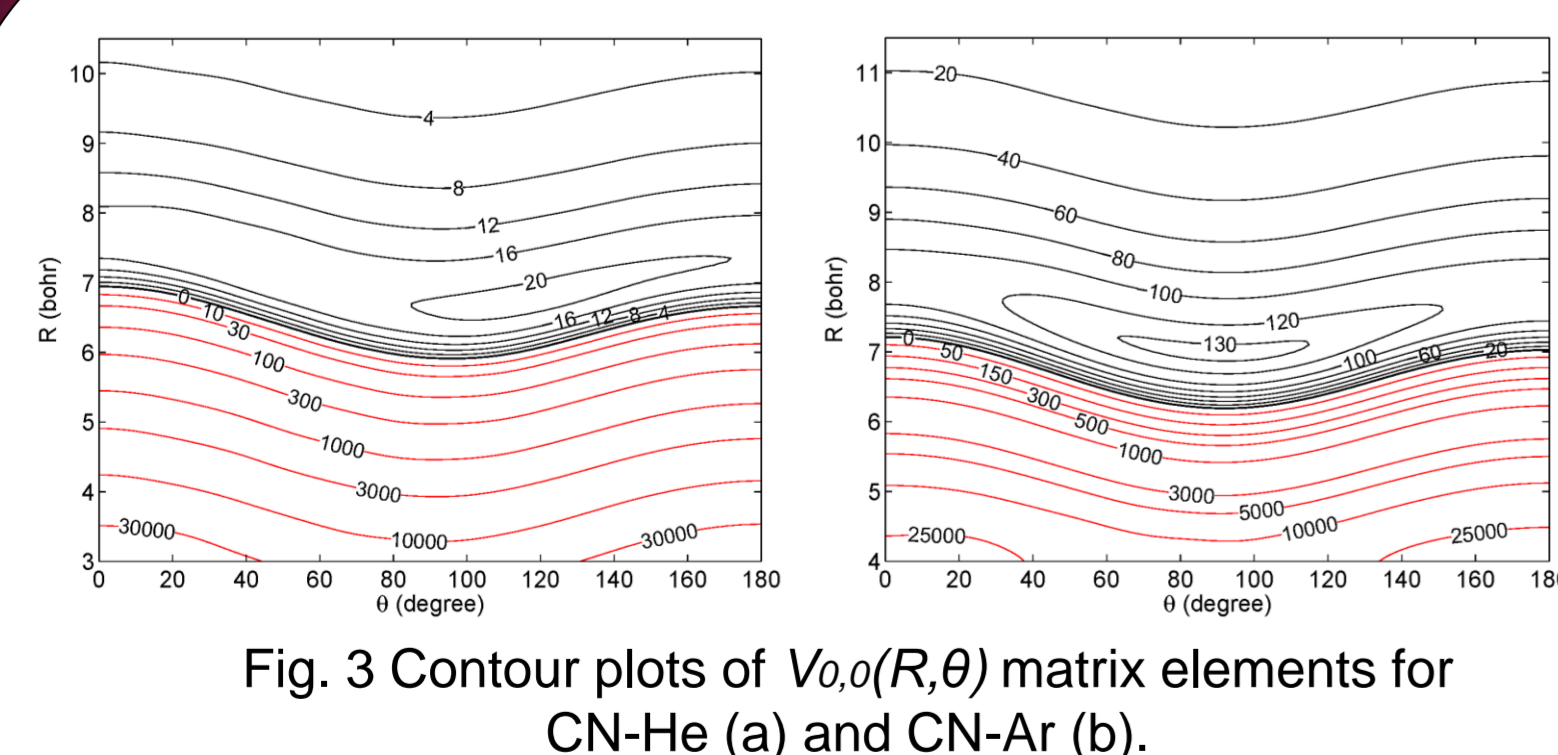


Fig. 3 Contour plots of $V_{0,0}(R, \theta)$ matrix elements for CN-He (a) and CN-Ar (b).

For VCC-IOs method matrix elements of the potential between the vibrational states of the CN molecule are required for fixed values of scattering angle θ and all the R -values.

$$V_{v,v'}(R, \theta) = \langle v | V(r, R, \theta) | v' \rangle$$

The coupling of $v=0$ and $v=1$ levels increases as the scattering coordinate R decreases (Fig. 5).

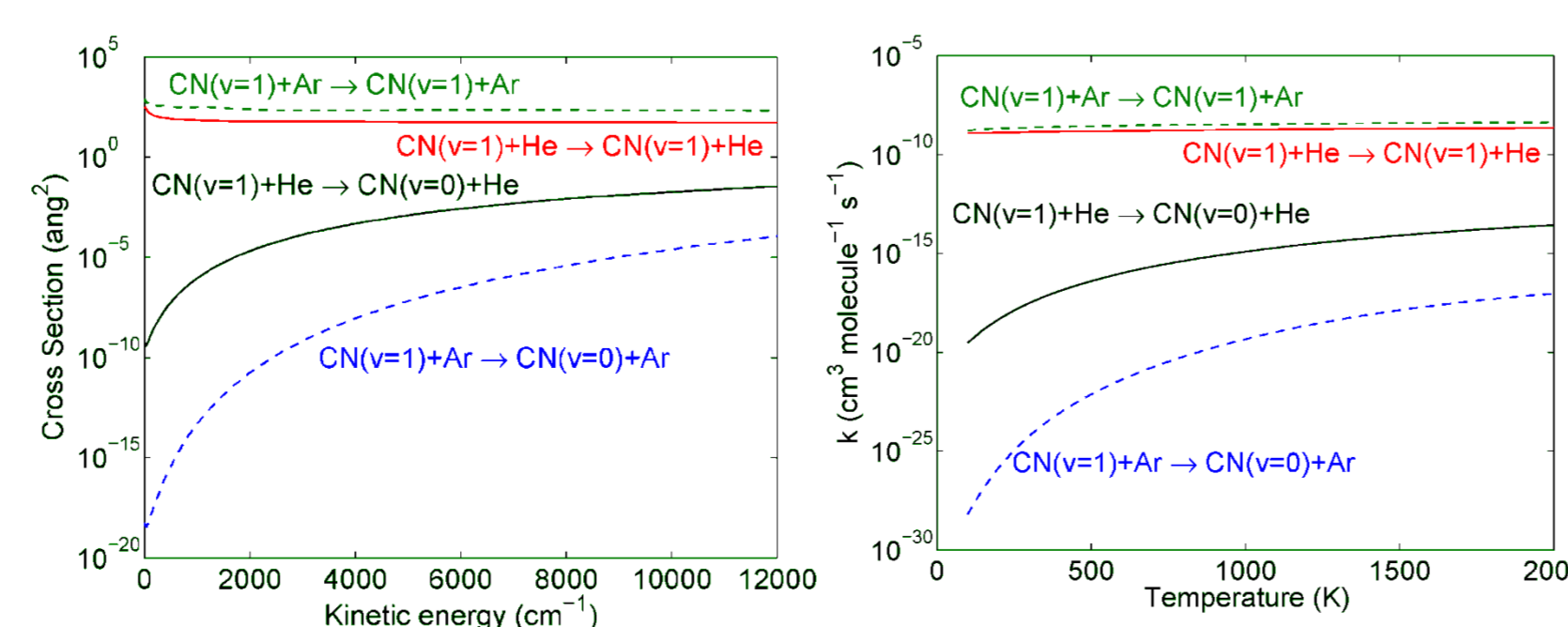


Fig. 5 Cross sections and rate coefficients for CN-He/Ar.

Elastic process clearly dominates the inelastic one for any T (Fig. 5) and the vibrational relaxation of CN($v=1$) by He is much faster than the vibrational relaxation of CN($v=1$) by Ar.

IRC+10216: for average temperature and density [13] and He abundance 0.2 of H_2 , $\tau \sim 100$ s (for relaxation with He) in the hottest and densest region. Even in this zone, τ is still a minimum of two orders of magnitude higher than the average time between collisions. Thus, the relaxation by He doesn't constitute a significant competitive channel.

The main collisional partner in circumstellar envelopes is H_2 . We can estimate, that rate coefficients for CN($v=1$)+ $H_2 \rightarrow$ CN($v=0$)+ H_2 will be larger then for CN($v=1$)+He \rightarrow CN($v=0$)+He (see, [14]) and, thus, may become a more competitive channel for the destruction of CN($v=1$) (for $T < 300$ K).

However, there are also reactive collisions of CN with H_2 : CN+ $H_2 \rightarrow$ HCN+H. At high temperatures (>1000 K) this pathway may be the dominant one leading to the destruction of CN($v=1$). This will be consistent with the fact that CN has not been observed in excited vibrational state in IRC+10216.

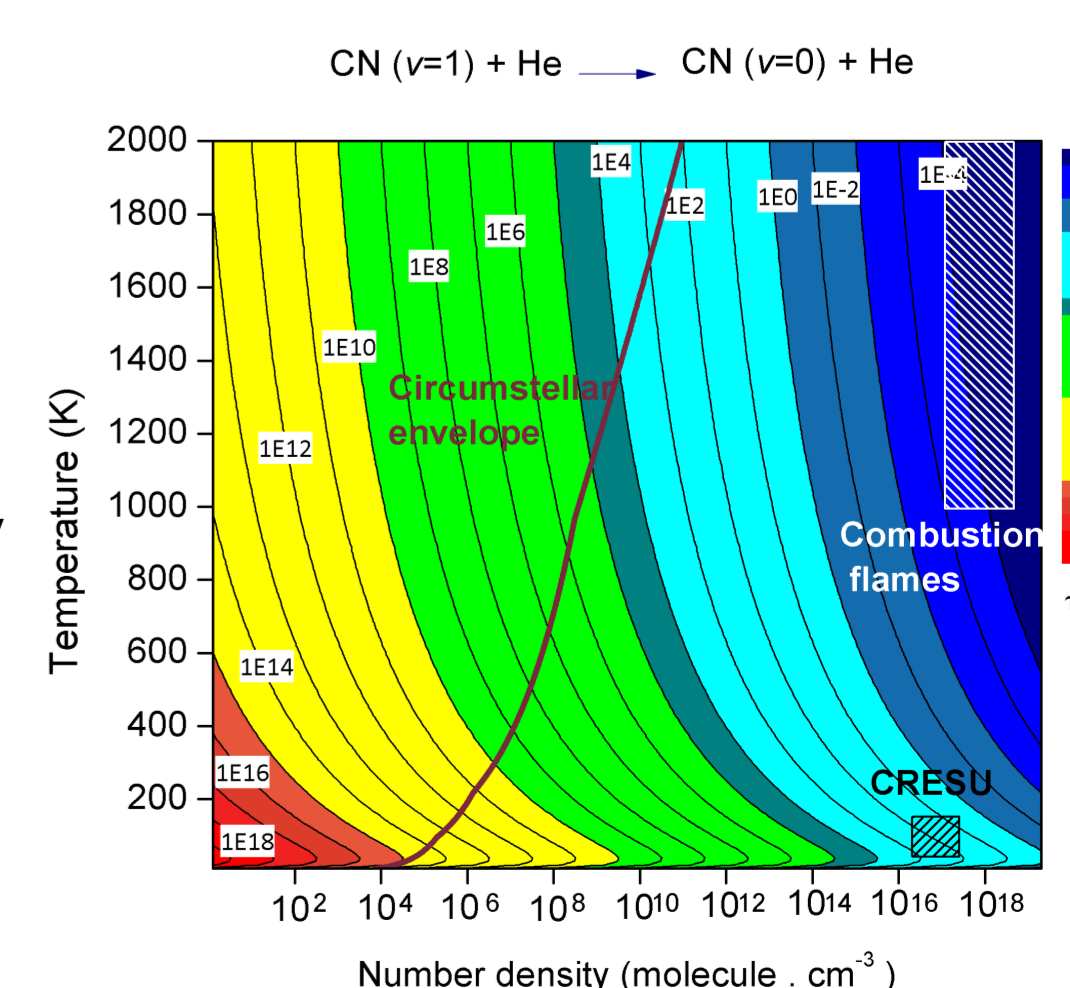


Fig. 6 Relaxation time τ of CN($v=1$) with He.

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Acknowledgements

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