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# Fine and hyperfine excitation of C<sub>2</sub>H by collisions with He at low temperature

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## ABSTRACT

Modelling of molecular emission from interstellar clouds requires the calculation of rate coefficients for excitation by collisions with the most abundant species. From a new, highly correlated, two-dimensional potential energy surface, rotational excitation of the C<sub>2</sub>H(X<sup>2</sup>Σ<sup>+</sup>) molecule by collision with He is investigated. State-to-state collisional excitation cross-sections between the 25 first fine structure levels of C<sub>2</sub>H are calculated for energies up to 800 cm<sup>-1</sup> which yields after thermal averaging rate coefficients up to  $T = 100$  K. The exact spin splitting of the energy levels is taken into account. The recoupling technique introduced by Alexander & Dagdigan allows us to deduce the corresponding temperature-dependent hyperfine state-to-state rate coefficients. Propensity rules are discussed.

**Key words:** line: formation – molecular data – molecular processes – scattering – ISM: molecules.

## 1 INTRODUCTION

The C<sub>2</sub>H ethynyl radical was one of the first radical detected in the interstellar medium (ISM) (Tucker, Kutner & Thaddeus 1974), then its rotational spectrum was studied in the laboratory at different millimetre and submillimetre wavelengths (Saastry et al. 1981; Gottlieb, Gottlieb & Thaddeus 1983; Müller, Klaus & Winnewisser 2000; Brünken et al. 2007). C<sub>2</sub>H is found to be one of the most abundant interstellar molecules in standard Galactic sources (e.g. Orion A, TMC-1) as well as in other type of sources including photodominated regions (Teyssier et al. 2004), diffuse clouds (Lucas & Liszt 2000), protoplanetary discs (Dutrey, Guilloteau & Guélin 1997), pre-stellar cores (Padovani et al. 2009) and high-mass star-forming regions (Beuther et al. 2008). In most sources, the abundance of CCH is only 2–3 times lower than that of formaldehyde. C<sub>2</sub>H isotopologues were detected in the ISM as well: CCD (Combes et al. 1985), <sup>13</sup>C<sub>2</sub>H and C<sup>13</sup>CH (Saleck et al. 1994).

The abundance of C<sub>2</sub>H is of particular interest in the context of chemistry of C-containing species. Moreover, its <sup>2</sup>Σ ground state gives rise to Zeeman splitting, so C<sub>2</sub>H was found to be a suitable molecule to determine magnetic fields (Bel & Leroy 1998). It is also of interest because hyperfine and spin interactions cause the rotational transitions to split into six (transition 1 → 0) or 11 (transitions  $N + 1 \rightarrow N$  with  $N > 0$ ) components which can be observed simultaneously.

Due to the low density of the ISM, the rotational levels of the molecules are not at local thermodynamical equilibrium. Thus modelling of molecular emission requires excitation calculations using radiative as well as collisional rate coefficients with the most abundant interstellar species He and H<sub>2</sub>. Recent studies (Daniel, Cernicharo & Dubernet 2006; Lique, Cernicharo & Cox 2006; Sarrasin et al. 2010) have shown that the degree of excitation of molecules crucially depends on the collisional rate coefficients.

To the best of our knowledge, no collisional data exist for collisional excitation of C<sub>2</sub>H(X<sup>2</sup>Σ<sup>+</sup>).

In this paper, we report fully quantum close-coupling calculations for the fine and hyperfine excitation rate coefficients of C<sub>2</sub>H with He. The results were obtained using a new accurate potential energy surface (PES). The details of the ab initio calculations of the C<sub>2</sub>H–He PES are presented in the next section. In Section 3, we report some theoretical aspects of the scattering calculations of state-to-state cross-sections and rate coefficients. Collisional rate coefficients between fine and hyperfine levels are presented in Section 4 for temperature up to 100 K. The results are discussed and propensity rules are given. Conclusions of the present work are given in Section 5.

## 2 POTENTIAL ENERGY SURFACE

### 2.1 Computational method

In the present study we consider the C<sub>2</sub>H radical as a rigid molecule, neglecting in particular possible excitation of the bending mode for

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energies larger than  $372\text{ cm}^{-1}$ , the energy of the ground vibrational state. The results obtained for ro-vibrational excitation of water by collisions with  $\text{H}_2$  suggest that decoupling between the rotational and bending modes is qualitatively correct (Faure & Josselin 2008). Similar conclusions were drawn for the stretching mode of the CS molecule in collision with He (Lique & Spielfiedel 2007). Neglecting the coupling between rotation and bending may lead to slightly overestimating the cross-sections when the bending channel is open. However, we may also consider that, due to the Boltzmann average of rotational cross-sections, energies larger than  $372\text{ cm}^{-1}$  contribute to a small amount of the total rate coefficients for low temperatures. We thus expect that the rigid-body approach employed here may lead to a maximum of a few per cent error on the collisional rate coefficients.

The  $\text{C}_2\text{H}(X^2\Sigma^+)$  molecule is linear, hence, in a rigid-body approach, the  $\text{C}_2\text{H}\text{--}\text{He}$  PES depends on two dimensions (2D) only. The 2D  $\text{C}_2\text{H}\text{--}\text{He}$  PES was calculated using the same procedure as that described for the  $\text{CN}\text{--}\text{He}$  PES by Lique et al. (2010). The  $\text{C}_2\text{H}\text{--}\text{He}$  system can be described by the usual Jacobi coordinates:  $R$ , the distance between the He atom and the centre of mass of the  $\text{C}_2\text{H}$  molecule;  $r = r_1 + r_2$  with  $r_1$  the C–C distance and  $r_2$  the C–H distance in the  $\text{C}_2\text{H}$  molecule, and  $\theta$ , the angle between  $R$  and  $r$ . The  $\text{C}_2\text{H}$  bond defines the  $z$ -axis and we assume that the  $\text{C}_2\text{H}\text{--}\text{He}$  system lies in the  $xz$  plane. For low-energy rotational excitation, we determined an accurate PES by means of partially spin-restricted coupled cluster calculations with single, double and perturbative triple excitations [RCCSD(T)] (Knowles, Hampel & Werner 1993, 2000). We kept the  $\text{C}_2\text{H}$  bond distances frozen at their experimental equilibrium geometries ( $r_1 = 2.299a_0$  and  $r_2 = 1.968a_0$ ) (Bogey, Demuyne & Destombes 1989). We used the aug-cc-pVQZ basis set of Woon & Dunning (1994) for the three atoms, augmented by the bond functions optimized by Cybulski & Toczyłowski (1999) placed at mid-distance between the  $\text{C}_2\text{H}$  centre of mass and He.

The electronic wavefunction which asymptotically correlates to the ground dissociation limit  $\text{C}_2\text{H}(X^2\Sigma^+)+\text{He}$  is of  $^2A'$  symmetry. The first excited electronic state of  $\text{C}_2\text{H}$  ( $A^2\Pi$  state) lies approximately  $5100\text{ cm}^{-1}$  above the ground state. In the presence of the He atom, the degeneracy of the  $A^2\Pi$  state is lifted, giving rise to two adiabatic electronic states of  $^2A'$  and  $^2A''$  reflection symmetry. As was previously found for the  $\text{CN}(X^2\Sigma^+)+\text{He}$  system (Lique et al 2010), the two  $^2A'$  states, which asymptotically correlate to  $\text{C}_2\text{H}(X^2\Sigma^+)+\text{He}$  and  $\text{C}_2\text{H}(A^2\Pi)+\text{He}$ , mix strongly when the  $\text{C}_2\text{H}$  bonds are stretched slightly beyond their equilibrium distances (Taroni & Carter 2003). To be sure to obtain the energy of the lowest  $^2A'$  state, we adopted the following strategy: after a restricted Hartree–Fock first step, we carried out complete active space self-consistent field (CASSCF) calculations for the lowest three electronic states, two of  $^2A'$  and one of  $^2A''$  symmetry. The calculation was performed using a set of nine molecular orbitals with the two  $1s(a')$  core orbitals doubly occupied. Of the seven active orbitals, the sole orbital of  $a''$  symmetry is doubly occupied in the two  $^2A'$  states and singly occupied in the  $^2A''$  state. From this common set of orbitals, we subsequently carried out RCCSD(T) calculations for the  $X^2A'$  state. All the quantum chemistry calculations were carried out using the MOLPRO 2006 package.<sup>1</sup> For all nuclear geometries considered,

<sup>1</sup> MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobyn, F. Eckert, C. Hampel, T. Leininger, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone and T. Thorsteinsson.

we checked that the dominant CASSCF configuration for the lowest  $^2A'$  state was greater than 0.9, to ensure that a single-reference description is valid.

At all geometries, the Boys & Bernardi (1970) counterpoise procedure was used to correct for basis set superposition error. In this procedure, the interaction energy is defined by

$$V(R, \theta) = E_{\text{C}_2\text{H--He}}(R, \theta) - E_{\text{C}_2\text{H}}(R, \theta) - E_{\text{He}}(R, \theta), \quad (1)$$

where the energies of the  $\text{C}_2\text{H}$  and He subsystems are determined with the full (atoms+bond functions) basis set. The calculations were done for a total of 684 geometries. The values of  $R$  ranged from 4.0 to 10.0 bohr in steps of 0.25, adding the values 10.5, 11, 11.5, 12, 13, 14, 15, 17.5, 20, 22.5 and 25 bohr. We used an uniform angular grid with points at every  $10^\circ$  spacing from  $0^\circ$  to  $180^\circ$ . In our convention,  $\theta = 0^\circ$  corresponds to He atom approaching to the carbon atom.

## 2.2 Analytical representation and features of the PES

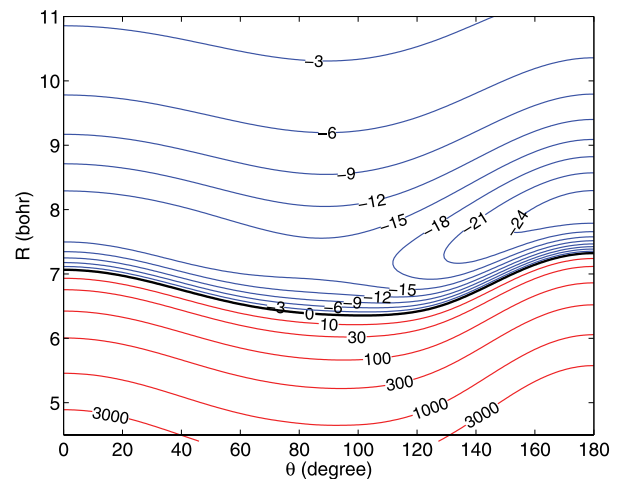
Fig. 1 shows a contour plot of the PES. For this weakly bound  $\text{C}_2\text{H}\text{--}\text{He}$  system, the global minimum of the interaction energy is  $-25.54\text{ cm}^{-1}$  at  $R = 8.006$  bohr and  $\theta = 180^\circ$ . As can be seen, the anisotropy of the PES is huge at short  $R$  distances.

As we aim to solve close-coupling equations for the scattering, we need to expand the 2D PES in terms of Legendre polynomials as follows:

$$V(R, \theta) = \sum_l V_l(R) P_l(\cos \theta). \quad (2)$$

We adapted the fitting procedure described by Werner et al. (1989) to obtain an analytic representation of the PES. We used an expansion involving 19 Legendre polynomials to represent the angular anisotropy. Over the entire grid, the mean relative error between the analytic fit and the ab initio points is 0.2 per cent.

Considering the strong anisotropy of the PES, we have checked the validity of the truncated analytic expansion of equation (2) by using an alternative fitting procedure based on the reproducing kernel Hilbert space (RKHS) method (Ho & Rabitz 1996). The resulting analytic RKHS PES was then projected on to Legendre polynomials (using Gauss–Legendre quadrature) to derive a new set of radial coefficients  $V_l(R)$ . It was found that both methods provide very similar  $V_l(R)$  coefficients, which is a stringent probe of the



**Figure 1.** Contour plot of the  $\text{C}_2\text{H}\text{--}\text{He}$  PES as a function of  $R$  and  $\theta$ .  $\theta = 0$  corresponds to co-linear  $\text{He}\text{--}\text{CCH}$ .

convergence of the polynomial expansion of equation (2). Regarding the validity of the long-range (LR) part of the PES, there is a lack of experimental and theoretical data to compare with. Nonetheless, accounting for the known<sup>2</sup> electrostatic properties of  $C_2H$  and He, we could derive a theoretical estimate for the dominant contribution to  $C_2H$ -He LR interactions, namely the dipole-induced dispersion and dipole-induced/dipole induction contributions, both giving rise to LR energies varying as  $R^{-6}$ . For the isotropic LR coefficients, we get  $C_{60}^{\text{disp}} = 12.9$  au and  $C_{60}^{\text{ind}} = 0.1$  au, and, for the anisotropic one, we found  $C_{62}^{\text{disp}} = 1.3$  au ( $C_{62}^{\text{ind}} = C_{60}^{\text{ind}}$ ). Assuming the following truncated expansion for the LR part of the radial coefficients,  $V_l(R) \approx -C_{6l}/R^6 - C_{8l}/R^8$  (with  $l = 0, 2$ ), the analytical PES yields isotropic  $C_{60} = 14.2$  au and anisotropic  $C_{62} = 1.4$  au LR coefficients which are consistent with the values derived from monomer properties (13.0 and 1.4 au, respectively).

### 3 SCATTERING CALCULATIONS

The main focus of this paper is the use of the newly calculated  $C_2H$ -He PES to determine excitation cross-sections and rate coefficients of  $C_2H$  molecules by collisions with He. For  $C_2H$  in the  $^2\Sigma^+$  state, the molecular levels can be described in the Hund's case (b) limit. Here, the fine structure levels are labelled by  $Nj$ , where  $N$  is the rotational angular momentum and  $j$  the total molecular angular momentum with  $j = N + S$ , where  $S$  is the electronic spin. For molecules in a  $^2\Sigma^+$  state,  $S = 1/2$ . The levels with  $j = N + 1/2$  are labelled 'e' and those with  $j = N - 1/2$ , labelled 'f'. The hydrogen atom also has a non-zero nuclear spin ( $I = 1/2$ ). The coupling between  $I$  and  $j$  results in a splitting of each level into two hyperfine levels. Each hyperfine level is designated by a quantum number  $F$  ( $F = I + j$ ) varying between  $|I - j|$  and  $I + j$ .

We used Alexander's theory (Alexander 1982) of inelastic scattering between an atom and a diatomic molecule in a  $^2\Sigma^+$  electronic state and fully quantum close-coupling calculations to obtain the  $S^J(jl; j'l')$  diffusion matrix elements between  $C_2H$  fine structure levels.  $J$  and  $l$  denote the total angular momentum ( $J = j + l$ ) and  $l$  the relative orbital angular momentum, respectively. Inelastic cross-sections associated with a transition from an initial level  $Nj$  to a final level  $N'j'$  were given by

$$\sigma_{Nj \rightarrow N'j'} = \frac{\pi}{k_{Nj}^2(2j+1)} \sum_K P^K(j \rightarrow j'). \quad (3)$$

The  $P^K(j \rightarrow j')$  are the tensor opacities defined by

$$P^K(j \rightarrow j') = \frac{1}{2K+1} \sum_{ll'} |T^K(jl; j'l')|^2, \quad (4)$$

where we have introduced the irreducible components of the nuclear spin-free  $T$ -matrix elements (where  $T = 1 - S$ ) defined by

<sup>2</sup>For  $C_2H$ , we used the theoretical dipole moment  $\mu = 0.28a_0$  and dipole polarizability (isotropic  $\bar{\alpha} : 21.39a_0^3$  and anisotropic  $\Delta\alpha = 6.54a_0^3$  components) computed by Duflot (private communication) from CASSCF/MRCI(Q) calculations with an aug-cc-pV5Z basis set. For He, we used the theoretical dipole polarizability of Bishop & Pipin (1993). For both systems, we employed the experimental ionization energies  $\eta$  tabulated in the National Institute of Standards and Technology (<http://webbook.nist.gov/chemistry>). The London approximation (Langhoff & Karplus 1970) was used to evaluate the dispersion interaction coefficients,  $C_{60}^{\text{disp}} \approx \frac{3}{2} \frac{\eta_a \eta_b}{\eta_a + \eta_b} \bar{\alpha}_a \bar{\alpha}_b$  and  $C_{62}^{\text{disp}} \approx \frac{1}{2} \frac{\eta_a \eta_b}{\eta_a + \eta_b} \bar{\alpha}_a \Delta\alpha_b$ . For a closed-shell atom+linear molecule system, the dipole-induced/dipole induction coefficient takes the form (Nielson, Parker & Pack 1976)  $C_{60}^{\text{ind}} = C_{62}^{\text{ind}} = \bar{\alpha}_a (\mu_b)^2$ .

Alexander & Davis (1983):

$$T^K(jl; N'l') = (-1)^{-j-l'} (2K+1) \sum_J (-1)^J (2J+1) \times \begin{Bmatrix} l' & j' & J \\ j & l & K \end{Bmatrix} T^J(jl; j'l'). \quad (5)$$

It is important to note that the calculation of the  $P^K$  tensor opacities implies cross terms with different  $J, J'$  total angular momenta.

Cross-sections between hyperfine levels may be deduced from the nuclear spin-free  $T$ -matrix elements using the recoupling method of Alexander & Dagdigian (1985). This approach is completely justified (Alexander & Dagdigian 1985) by the very small splitting of the levels due to the hyperfine interactions ( $b$  and  $c$  hyperfine constants equal to 0.001 484 and 0.000 408  $\text{cm}^{-1}$ , respectively; Killian, Gottlieb & Thaddeus 2007). Inelastic cross-sections associated with a transition from an initial hyperfine level  $NjF$  to a final hyperfine level  $N'j'F'$  were thus obtained as follow:

$$\sigma_{NjF \rightarrow N'j'F'} = \frac{\pi}{k_{NjF}^2} (2F'+1) \sum_K \times \begin{Bmatrix} j & j' & K \\ F' & F & I \end{Bmatrix}^2 P^K(j \rightarrow j'). \quad (6)$$

All the scattering calculations were performed with the HIBRIDON package.<sup>3</sup>

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

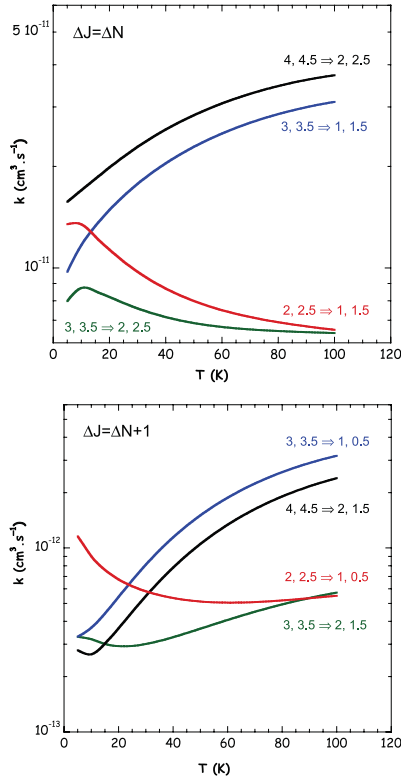
$$k_{NjF \rightarrow N'j'F'}(T) = \left( \frac{8}{\pi\mu(k_B T)^3} \right)^{1/2} \times \int_0^\infty \sigma_{NjF \rightarrow N'j'F'}(E_c) e^{-\frac{E_c}{kT}} dE_c, \quad (7)$$

where  $k$  is Boltzmann's constant and the integral extends over all values of the collision energy.

In all the scattering calculations, the propagation was performed from 3.5 to 60 bohr. The energy levels were computed from the following spectroscopic constants for  $C_2H$ :  $B_0 = 1.456\,825\text{ cm}^{-1}$ ,  $D_0$  (the centrifugal distortion constant)  $= 3.589\,10^{-6}\text{ cm}^{-1}$  and the spin-splitting constant  $\gamma_0 = -0.002\,089\,678\text{ cm}^{-1}$ . The rotational basis of  $C_2H$  included all states up to  $N = 12$  for total energies up to 50  $\text{cm}^{-1}$ ,  $N = 14$  for total energies in the range between 50 and 100  $\text{cm}^{-1}$ ,  $N = 16$  for total energies in the range between 100 and 200  $\text{cm}^{-1}$ ,  $N = 18$  for total energies in the range between 200 and 300  $\text{cm}^{-1}$ ,  $N = 20$  for energies up to 800  $\text{cm}^{-1}$ . At each collision energy, the total angular momentum  $J$  was set large enough that the cross-sections were converged within 0.01  $\text{\AA}^2$ , the value of  $J$  varies from 75 at low energies to 120 for energies larger than 300  $\text{cm}^{-1}$ . These large values of  $J$  are required to obtain fully converged  $NjF \rightarrow N'j'F'$  cross-sections given in terms of elastic spin-free  $T$ -matrix elements.

We carefully spanned the energy range to take into account the presence of resonances. The energy steps are 0.2  $\text{cm}^{-1}$  below 50  $\text{cm}^{-1}$ , 0.5  $\text{cm}^{-1}$  from 50 to 100  $\text{cm}^{-1}$ , 1.0  $\text{cm}^{-1}$  from 100 to

<sup>3</sup>The HIBRIDON package was written by M. H. Alexander, D. E. Manolopoulos, H.-J. Werner and B. Follmeg, with contributions from P. F. Vohralik, D. Lemoine, G. Corey, R. Gordon, B. Johnson, T. Orlikowski, A. Berning, A. Degli-Esposti, C. Rist, P. Dagdigian, B. Pouilly, G. van der Sanden, M. Yang, F. de Weerd, S. Gregurick, J. Kłos and F. Lique (<http://www2.chem.umd.edu/groups/alexander/>).



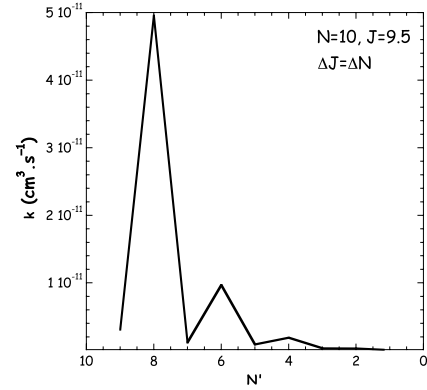
**Figure 2.** Temperature variation of de-excitation rate coefficients for transitions  $N, j \rightarrow N', j'$  with  $\Delta N = 1, 2$  and  $\Delta j = \Delta N$  (upper panel) and  $\Delta j = \Delta N + 1$  (lower panel).

$300 \text{ cm}^{-1}$ ,  $2.0 \text{ cm}^{-1}$  from  $300$  to  $500 \text{ cm}^{-1}$ . Moreover, calculations at  $550, 600, 650, 700, 750$  and  $800 \text{ cm}^{-1}$  were performed in order to obtain converged rate coefficients for temperatures up to  $100 \text{ K}$ . The complete sets of (de-)excitation rate coefficients with  $N, N' \leq 12$  will be made available online at the LAMDA<sup>4</sup> (Leiden Atomic and Molecular Database, Shöier et al. 2005) and BASECOL<sup>5</sup> (Ro-vibrational COLLision excitation dataBASE and utilities, Dubennet et al. 2004) websites.

## 4 RESULTS

### 4.1 Excitation of the fine structure levels

Fig. 2 presents the variation with temperature of de-excitation rate coefficients for selected  $N - N' = 1, 2$  transitions. We observe a strong propensity for  $\Delta j = \Delta N$  transitions, the corresponding rate coefficients being larger (by a factor up to 10) than coefficients for  $\Delta j \neq \Delta N$ . This behaviour, predicted theoretically (Alexander, Smedley & Corey 1986) for collisions of molecules in  $2S+1\Sigma$  electronic state in collision with rare gases, was found for many other systems like SO (Lique et al. 2005), CN (Lique et al. 2010), O<sub>2</sub> (Lique 2010) and NH (Tobola et al. 2011). We also notice a propensity for transitions with even  $\Delta N$ , mainly  $\Delta N = 2$ . This effect is well illustrated in Fig. 3, which displays the de-excitation rate coefficients  $k_{Nj \rightarrow N'j'}$  at temperature  $T = 50 \text{ K}$  out of level  $N = 10, j = 9.5$  for  $\Delta j = \Delta N$  transitions. Such propensity is a consequence of the near-homonuclear symmetry of the PES. This effect

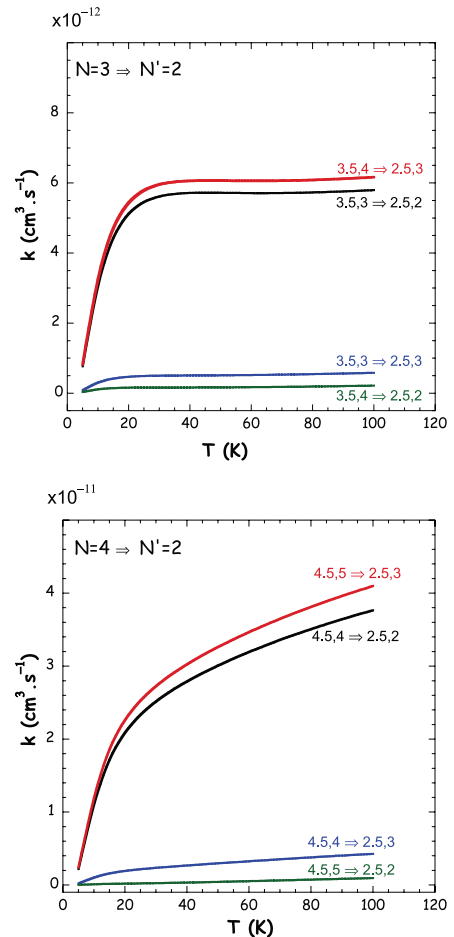


**Figure 3.** Inelastic de-excitation rate coefficients at  $50 \text{ K}$  out of  $N = 10, j = 9.5$ .

is well known experimentally and was first explained by McCurdy & Miller (1977).

### 4.2 Hyperfine excitation of C<sub>2</sub>H by He

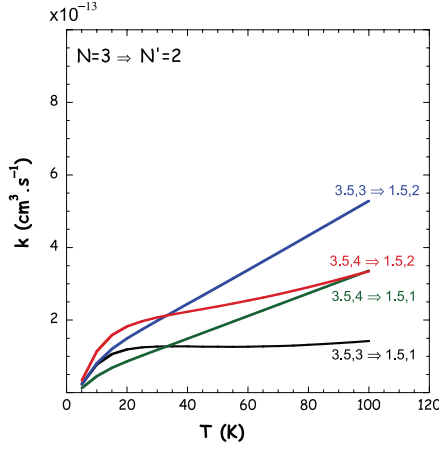
Using the computational scheme described in equation (6), we have obtained inelastic cross-sections for C<sub>2</sub>H transitions between the



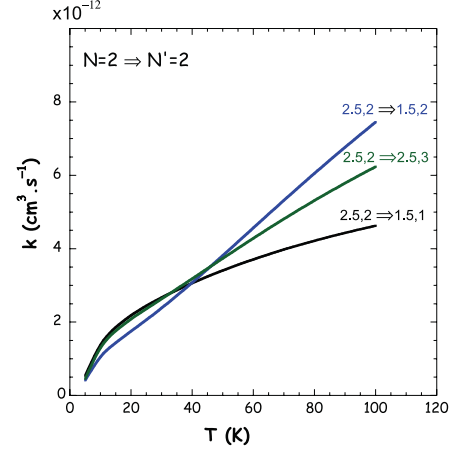
**Figure 4.** Temperature variation of hyperfine resolved C<sub>2</sub>H-He rate coefficients for  $N = 3, J, F \rightarrow N' = 2, j', F'$  (upper panel),  $N = 4, J, F \rightarrow N' = 2, j', F'$  (lower panel) and  $\Delta j = \Delta N$  transitions.

<sup>4</sup> <http://www.strw.leidenuniv.nl/~moldata/>

<sup>5</sup> <http://basecol.obspm.fr/>



**Figure 5.** Temperature variation of hyperfine resolved  $C_2H$ -He rate coefficients for  $N = 3, J, F \rightarrow N' = 2, j', F'$  and  $\Delta j = \Delta N + 1$  transitions.



**Figure 6.** Temperature variation of rate coefficients for  $N = 2, J = 2.5, F = 2 \rightarrow N = 2, j', F'$  transitions.

50 first hyperfine levels with  $N, N' \leq 12$ . Rate coefficients were calculated for temperatures up to 100 K.

Figs 4 and 5 present the temperature dependence of the de-excitation hyperfine resolved  $C_2H$ -He rate coefficients for selected  $N = 3, 4, J, F \rightarrow N' = 2, j', F'$  transitions, with  $\Delta j = \Delta N$  and  $\Delta j = \Delta N + 1$ , respectively. Table 1 displays  $N = 4, jF \rightarrow N' = 2, 3, j'F'$  rate coefficients at 50 K.

From these figures and Table 1, one can see propensity for  $\Delta N = 2$  and  $\Delta j = \Delta N$  transitions, as was already found for fine structure collision rate coefficients. Moreover, for those transitions a strong propensity in favour of  $\Delta j = \Delta F$  transitions is observed, this trend increases with increasing  $N$ . The same trends, predicted theoretically by Alexander & Dagdigian (1985) and Corey & Alexander (1988), were obtained recently for  $CN$ -He collisions by Lique & Klos (2011). For  $\Delta j \neq \Delta N$  transitions, no clear propensity rule appears. In particular, the rate coefficients are not proportional to the degeneracy ( $2F' + 1$ ) of the final hyperfine level.

Fig. 6 presents the temperature variation of the rate coefficients for the quasi-elastic  $N = 2, J = 2.5, F = 2 \rightarrow N = 2, j', F'$  transitions. The order of magnitude of those coefficients is relatively large, without clear trend of temperature-independent propensity.

## 5 SUMMARY AND CONCLUSION

We have used quantum scattering calculations to investigate rotational energy transfer of  $C_2H$  in collisions with He atoms. The calculations are based on a new, highly correlated 2D PES calculated at the RCCSD(T) level using large basis sets. Close-coupling calculations were obtained for collision energies ranging from 0 to  $800 \text{ cm}^{-1}$ , the fine structure splitting of the levels was explicitly

taken into account. Rate coefficients for transitions involving the lowest 25 fine structure levels of the  $C_2H$  molecule were determined for temperatures ranging from 1 to 100 K. Hyperfine state-resolved rate coefficients for transitions involving the same levels were obtained through the recoupling technique of Alexander & Dagdigian (1985).

The fine structure rate coefficients show strong propensity for even  $\Delta N$  and  $\Delta j = \Delta N$  transitions. Considering transitions between hyperfine levels, the collisions exhibit propensity rules in favour of  $\Delta F = \Delta j$  transitions for  $\Delta j = \Delta N$  and no systematic trend is observed for the other transitions. We conclude that approximate random methods cannot work for excitation of the  $C_2H$  hyperfine levels by collision with He.

Finally, the large abundance of  $H_2$  in the ISM makes this molecule the primary collision partner for all the species. It is generally assumed that rate coefficients with He can provide a good estimate of rate coefficients with para- $H_2(j = 0)$ . Results on the rotational excitation of CO (Wernli et al. 2006), SiS (Lique et al. 2008) and HNC (Dumouchel, Faure & Lique 2010; Dumouchel, Klos & Lique 2011) show that rate coefficients for collisions with para- $H_2(j = 0)$  can be up to a factor of 3 larger or smaller than those for collisions with He, depending on the transition, but the He rate coefficients give a correct order of magnitude of the para- $H_2(j = 0)$  rate coefficients. However, recent work on  $SO_2$  in collision with para- and ortho- $H_2$  (Cernicharo et al. 2011) shows large differences between the rate coefficients relative to the two partners, so it seems unadvisable to use the present He rate coefficients as an estimate of ortho- $H_2$  rate coefficients. Specific calculations with ortho- $H_2$  must be performed.

**Table 1.** Hyperfine resolved  $C_2H$ -He de-excitation rate coefficients ( $\times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) for  $N = 4, j, F \rightarrow N' = 2, 3, j', F'$  transitions at 50 K.

		$N' = 3$	$N' = 3$	$N' = 3$	$N' = 3$	$N' = 2$	$N' = 2$	$N' = 2$	$N' = 2$
		$j' = 2.5$	$j' = 2.5$	$j' = 3.5$	$j' = 3.5$	$j' = 1.5$	$j' = 1.5$	$j' = 2.5$	$j' = 2.5$
		$F' = 2$	$F' = 3$	$F' = 3$	$F' = 4$	$F' = 1$	$F' = 2$	$F' = 2$	$F' = 3$
$j = 3.5$	$F = 3$	4.79	0.40	0.24	0.18	18.86	3.85	2.11	1.25
	$F = 4$	0.12	5.07	0.14	0.28	0.47	22.2	0.85	2.51
$j = 4.5$	$F = 4$	0.13	0.17	4.78	0.30	0.48	0.80	30.08	2.98
	$F = 5$	0.12	0.18	0.13	4.95	0.48	0.80	0.44	32.63

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