Inelastic rate coefficients for collisions of C_4H^- with para- $\text{H}_2(j = 0)$ at low temperatures

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ABSTRACT

Anions are very reactive species that can play important roles in the chemical evolution of the interstellar medium. Following the detection of C_6H^- carbon chains, investigations on detectable anions led to the discovery of five new species during the last decade. The C_4H^- anion was first observed in the circumstellar envelope of IRC + 10216 and in TMC-1. In these cool and low-density regions, an accurate modelling of the chemical and physical conditions of the observed emission lines requires the knowledge of both radiative and collisional excitation rates. We present here the first interaction potential energy surface and inelastic rate coefficients for C_4H^- in collision with para- $\text{H}_2(j_2 = 0)$. The *ab initio* interaction energies were computed using highly correlated coupled cluster procedures. Quantum scattering calculations were performed with the *ab initio* potential energy surface. The close-coupling approach was used to compute rotational excitation cross-sections of C_4H^- for the first 21 j_1 rotational levels (up to $j_1 = 20$) and for collisional energies up to 500 cm^{-1} . State-to-state rate coefficients were obtained for the temperature range 2–100 K.

Key words: molecular data – molecular processes – scattering.

1 INTRODUCTION

Collisional properties of molecules, such as rate coefficients for collision-induced rotational energy transfer, are crucial for the modelling of emission lines observed with the radioastronomical instruments. Modelization of the chemical and physical conditions in various astrophysical environments needs to interpret emission spectra through radiative transfer calculations which require the knowledge of both radiative and collisional excitation rates. The collisional data can be predicted theoretically, or, in few cases, derived from laboratory experiments (Roueff & Lique 2013). For most interstellar species, the unique existing information was obtained from theoretical approaches based on quantum chemistry and dynamics calculations.

This paper is devoted to the collisional excitation of the C_4H^- anion by para- H_2 . Anions are very reactive species that can play important roles in the chemical evolution of the interstellar medium (ISM) and on the free electron density that affects star formation

rates. Large carbon anions are formed through electron radiative attachment of their neutral counterpart, and are destroyed by reactions with H atoms (Agúndez, Cernicharo & Guélin 2015; Millar, Walsh & Field 2017). Although their presence in the ISM was predicted very early (Dalgarno & McCray 1973; Herbst 1981), the first detection of a negative species, the C_6H^- linear carbon chain, is relatively recent (McCarthy et al. 2006). The discovery encouraged the search of more interstellar anions and new laboratory inquiries focused on the most likely detectable anions (Bierbaum 2011). From 2006 to 2010, five more negative charged species, were detected: C_4H^- (Cernicharo et al. 2007; Agúndez et al. 2008; Sakai, Sakai & Yamamoto 2008), C_8H^- (Brünken et al. 2007; Kawaguchi et al. 2007; Remijan et al. 2007), CN^- (Agúndez et al. 2010), C_3N^- (Thaddeus et al. 2008), and C_5N^- (Walsh et al. 2009). Since 2010, the search has been fruitless and the detected species list has not been updated.

All the six detected anions are hydrogen-terminated or nitrogen-terminated linear carbon chains and show singlet ground electronic state of $^1\Sigma^+$ symmetry. C_4H^- was observed in the circumstellar envelope of IRC + 10216 through five lines corresponding to the $\Delta j_1 = 9-8, 11-10, 12-11, 14-13$, and $15-14$ rotational transitions (Cernicharo et al. 2007). The abundance of C_4H^-

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in IRC + 10216 was estimated to be 1/6 of the abundance of C_6H^- and 1/4200 of that of C_4H . The anion was also confirmed in L1527 (Agúndez et al. 2008) and detected in other sources such as the low-mass protostar IRAS 04368+2557 in L1527 (Sakai et al. 2008) and the ionosphere of Titan (Desai et al. 2017).

Although electron attachment can carry out important changes of the structures and physical properties of molecules, the structures of the carbon chain anions are generally very similar to that of the parent neutral radicals. C_4H^- and C_4H show linear geometries in their ground electronic states (McCarthy et al. 1995; Botschwina & Oswald 2008). The neutral pattern C_4H was earlier detected and experimentally characterized in 1998 (Shen, Doyle & Graham 1990). Taylor, Xu & Neumark (1998) analysed the photoelectron spectra determining the electronic and the vibrational structure. The adiabatic electron affinity was estimated to be 3.558 ± 0.015 eV. Photodetachment spectroscopy measurements in the vicinity of their electron detachment thresholds (Grutter, Wyss & Maier 1999; Pino et al. 2002) allowed to characterize the $^1\Pi$ dipole bound state in gas phase. The rotational spectrum was recorded and analysed by Gupta et al. (2007), and the rotational and centrifugal distortion constants were obtained ($B_0 = 4654.9449(2)$ MHz and $D_e = 0.5875 \times 10^{-3}$ MHz). C_4H^- was detected by Amano (2008) in electrical discharge in the submillimeter-wave region for transitions up to $j_1 = 54-53$, and rotational constants were derived. The spectroscopy and structure of the C_4H^- anion has been studied using theoretical methods. The studies of Botschwina & Oswald (2008) and Senent & Hochlaf (2010) provided detailed rovibrational parameters. Parity rules can be applied to understand the nature of the anionic electronic states and their participation in the formation of negatively charged heterogeneous carbon chains from carbon clusters (Senent & Hochlaf 2013).

To our knowledge, there is no collisional data available for C_4H^- . Some studies were conducted on the collisional excitation of the anionic carbon chains C_2H^- (Dumouchel et al. 2012) and C_6H^- (Walker et al. 2016, 2017), and their parent neutral radicals C_2H (Spielfiedel et al. 2012; Najar et al. 2014) and C_6H (Walker, Lique & Dawes 2018), with He or H_2 as colliders. The results showed that, for a given collider, the collisional rate coefficients of the anion and its neutral parent are of similar order of magnitude, but have a different temperature dependence and can differ by a factor of $\sim 2-3$ for the main Δj_1 rotational transitions. These results indicate different excitation mechanisms for the anion and neutral radical, and that collisional rates specific to each species are needed for a proper modelling of their molecular abundances. For C_4H^- and C_4H it will be challenging to compare the collisional rates since the scattering problem for C_4H involves taking into account four interacting electronic states lying at low energy (Senent & Hochlaf 2010).

In this paper we report the first interaction potential energy surface (PES) and inelastic rate coefficients for C_4H^- in collision with para- H_2 ($j_2 = 0$). The *ab initio* PES was computed using highly correlated coupled cluster procedures. Quantum scattering calculations based on the close-coupling (CC) method were performed to compute rotational excitation rate coefficients for the first 21 rotational levels of C_4H^- and temperatures up to 100 K. Details of the electronic structure calculations are given in Section 2.1 while Section 2.2 describes the surface fitting procedure. Section 3 provides a brief description of the scattering calculations. Section 4 presents collisional cross-sections and rate coefficients; conclusions are given in Section 5.

Table 1. C_4H^- rotational energy levels obtained from the experimental rotational constants of Amano (2008).

j_1	ϵ_{j_1} (cm $^{-1}$)	j_1	ϵ_{j_1} (cm $^{-1}$)
0	0.000	13	28.259
1	0.311	14	32.606
2	0.932	15	37.264
3	1.863	16	42.232
4	3.105	17	47.511
5	4.658	18	53.10
6	6.521	19	59.000
7	8.695	20	65.211
8	11.179	21	71.731
9	13.974	22	78.562
10	17.080	23	85.704
11	20.496	24	93.156
12	24.222	25	100.918

Figure 1. Jacobi coordinates (R , θ_1 , θ_2 , Φ) used for the $C_4H^-H_2$ collisional system and fixed internuclear distances of the C_4H^- and H_2 molecules. Distances are in Å.

2 COMPUTATIONAL METHODOLOGY

2.1 Ab initio calculations for the $C_4H^-H_2$ PES

Since this work primarily focuses on the rotational excitation of C_4H^- at low temperature, both monomers were considered as rigid species to deal with a reduced number of degrees of freedom. The lowest bending mode of C_4H^- , ν_7 , equal to 214 cm $^{-1}$ (Senent & Hochlaf 2010), is well above the energy of the highest C_4H^- rotational level considered in this work ($j_1 = 25$, see Table 1). Under such circumstances, even if the range of collision energies passes the threshold for excitation of this bending mode, the results of previous studies (Denis-Alpizar et al. 2013) suggest that the vibrational motion of C_4H^- should barely affect the pure rotational excitation process. The internuclear distance of H_2 was fixed at $r_{HH} = 0.76664$ Å, corresponding to the vibrationally averaged bond distance for para- H_2 ($j_2 = 0$). The geometry of the C_4H^- molecule (see Fig. 1) was optimized by means of *ab initio* quantum chemistry calculations, using the coupled-cluster method at the CCSD(T) level

Figure 2. Contour plot of the C_4H^- — H_2 PES as a function of R and θ_1 for a fixed orientation of the H_2 molecule, $(\theta_2, \Phi) = (0,0)$. The linear geometry $\theta_1 = 0^\circ$ corresponds to H_2 interacting with the C-end of C_4H^- . Interaction energies are in cm^{-1} .

of theory and the augmented correlation-consistent quintuple zeta (AV5Z) basis set.

The interaction potential was expressed in Jacobi coordinates $V(R, \theta_1, \theta_2, \Phi)$, where R is the distance between the C_4H^- and H_2 centres of mass. The polar angles of C_4H^- and H_2 with respect to the z -axis that coincides with $\mathbf{R}$ are denoted, respectively, by θ_1 and θ_2 , while Φ denotes the dihedral angle between half-planes containing the C_4H^- and H_2 bonds. The bond distances and Jacobi coordinates are displayed in Fig. 1. With the chosen convention, $\theta_1 = 0^\circ$ corresponds to H_2 approaching the C end of C_4H^- .

Following the strategy developed by Wernli and Valiron (Wernli 2006) for HC_3N — H_2 , the PES was calculated for five selected independent (θ_2, Φ) orientations of H_2 , hereafter labelled as $a_1 = (0, 0)$, $a_2 = (\pi/2, 0)$, $a_3 = (\pi/2, \pi/2)$, $a_4 = (\arccos(1/\sqrt{3}), \pi/4)$, and $a_5 = (\pi - \arccos(1/\sqrt{3}), \pi/4)$. For each of these five H_2 orientations, the $V(R, \theta_1; \theta_2, \Phi)$ PES was built on a 2D grid of (R, θ_1) coordinates, with θ_1 varying from 0° to 180° by steps of 10° , and R ranging from 3.5–6.5 bohr (depending on θ_1 value) up to 100 bohr. A total of 4235 geometries were computed for the five $V(R, \theta_1; \theta_2, \Phi)$ PESs.

The *ab initio* calculations were performed for the ground electronic state of C_4H^- — H_2 using the coupled-cluster method at the CCSD(T) level of theory, and including the usual counterpoise correction for the basis set superposition error (Boys & Bernardi 1970). We used the augmented correlation-consistent triple zeta (aVTZ) atomic basis sets (Woon & Dunning 1994) to describe C_4H^- . In order to avoid any possible steric hindrance, we did not use bond functions. Instead, as was previously discussed in the HC_3N — H_2 case (Wernli et al. 2007a), we choose the larger quadrupole zeta (aVQZ) basis set to better represent the highly polarizable H_2 target. The ensemble of both basis sets are denoted by (aVQZ/aVTZ). The accuracy of the present (CCSD(T)/aVQZ/aVZ) approach with regards to other levels of calculations is discussed in the Appendix. All *ab initio* calculations have been carried out with the molpro 2012 suite of programs (Werner et al. 2012).

We display in Figs 2 and 3 contour plots of the C_4H^- — H_2 PES $V(R, \theta_1, \theta_2, \Phi)$ for two selected orientations of the H_2 molecule (a_1 and a_2 geometries). The global minimum of the PES was found to be -780.27 cm^{-1} for $R = 9.5$ bohr and $\theta_1 = \theta_2 = \Phi = 0^\circ$, corresponding to a collinear orientation of the two monomers with H_2 interacting with the C-end of C_4H^- (Fig. 2). This minimum is not present for other H_2 orientations, while minima were found for

Figure 3. Contour plot of the C_4H^- — H_2 PES as a function of R and θ_1 for a fixed orientation of the H_2 molecule, $(\theta_2, \Phi) = (\pi/2, 0)$. Interaction energies are in cm^{-1} .

all H_2 orientations around $R = 6$ bohr and $\theta_1 = \pi/2$. The C_6H^- — H_2 PES (Walker et al. 2016) shows a behaviour which is qualitatively similar to the one observed for C_4H^- — H_2 , except for the presence of two minima around $\theta_1 = \pi/2$ for the $(\theta_2, \Phi) = (\pi/2, 0)$ geometry.

2.2 Average over H_2 orientations

As shown by Wernli et al. (2007a) in a study of HC_3N — H_2 collisions, if the dependence of the PES on H_2 orientations is sufficiently weak, a four-dimensional (4D) PES $V(R, \theta_1, \theta_2, \Phi)$ can be obtained from the five computed sets a_i ($i = 1 - 5$) of H_2 orientations (θ_2, Φ) , thus allowing to take into account the rotational motion of H_2 during the collisional process. However, this approximation is not expected to be justified for the C_4H^- — H_2 interaction, as can be seen from Figs 2 and 3 where the PES features strongly change with H_2 orientation. In the case of the C_6H^- — H_2 system (Walker et al. 2016), for which the PES behaves similarly to the present one, it was found necessary to include relatively high-order anisotropic terms with regards to H_2 orientations into the PES angular expansion. Nevertheless, the rotational motion of H_2 was found to barely influences the rotational excitation of C_6H^- by para- H_2 ($j_2 = 0$), as the inclusion of H_2 rotational levels higher than H_2 ($j_2 = 0$) led to excitation cross-sections that change by less than 10 per cent (Walker et al. 2017). Such a small dependence of the collisional excitation process on the H_2 rotational basis set was also observed for HC_3N (Wernli et al. 2007a,b; Faure, Lique & Wiesenfeld 2016) and HCO^+ (Massó & Wiesenfeld 2014). In the latter case, the HCO^+ — H_2 excitation rate coefficients calculated with a 4D PES and including H_2 ($j_2 = 0, 2$) in the basis set were found to differ by less than 5 per cent from the results obtained from a 2D PES averaged over H_2 orientations (Yazidi, Ben Abdallah & Lique 2014). These results indicate a small influence of H_2 rotation on the collisional excitation of long-chain ionic systems. Thus, in order to treat the rotational excitation of C_4H^- by para- H_2 ($j_2 = 0$), we chose to consider only the ground rotational level H_2 ($j_2 = 0$). In such a case, only the isotropic part of the PES with regards to H_2 orientations contributes to the excitation process (Najar et al. 2014), and the 4D PES $V(R, \theta_1, \theta_2, \Phi)$ can be reduced to a two-dimensional (2D) one $V_{\text{av}}(R, \theta_1)$ by averaging over the angular motion (θ_2, Φ) of H_2 .

From the five *ab initio* PESs $V(R, \theta_1; \theta_2, \Phi)$ computed at selected H_2 orientations, the 2D PES $V_{\text{av}}(R, \theta_1)$ is calculated as (Wernli

2006)

$$V_{av} = \frac{1}{7} [V_{a1} + V_{a2} + V_{a3} + 2(V_{a4} + V_{a5})], \quad (1)$$

where the dependence of each PES on (R, θ_1) has been omitted for the sake of conciseness. In order to solve the collisional problem, we need to expand the 2D PES over a set of suitable angular functions:

$$V_{av}(R, \theta_1) = \sum_{l_1} v_{l_1}(R) P_{l_1}(\cos \theta_1), \quad (2)$$

where $P_{l_1}(\cos \theta_1)$ are Legendre polynomials and the expansion coefficients $v_{l_1}(R)$ are the coupling terms that drive the rotational energy transfers. However, the latter expansion fails to converge for the present system due to the strong anisotropy of the PES with regards to C_4H^- orientations. We thus chose to follow an alternative procedure.

In a first step, we employed the reproducing kernel Hilbert space (RKHS) method (Ho & Rabitz 1996) to build an analytical representation of the 2D PES. The RKHS method was chosen as it can provide an accurate representation of the *ab initio* data, globally smooth (without spurious oscillations between the sampled data points), and having the correct long-range behaviour. The PES was expanded over a product of 1D functions as

$$V_{av}(x, y) = \sum_i^{N_R} \sum_j^{N_{\theta_1}} \alpha_{ij} q_{2,1}^{RP}(x_i, x) q_2^{TS}(y_j, y), \quad (3)$$

where (x, y) relate to the (R, θ_1) Jacobi coordinates as $x = R^2$ and $y = \theta_1/180$, and $N_R = 47$ and $N_{\theta_1} = 19$ are the number of *ab initio* data points for each coordinate. The 1D functions $q_{2,1}^{RP}(x_i, x)$ and $q_2^{TS}(y_j, y)$ are reciprocal-power (RP) and Taylor-spline (TS) reproducing kernels (Hollebeek, Ho & Rabitz 1999), respectively. The parameters chosen for the RP function lead to an analytical PES which behave asymptotically as $-C_4(\theta_1)/R^4 - C_6(\theta_1)/R^6$, consistent with the charge/dipole-induced and dispersion contributions to long-range interactions which remain after averaging over the angular motion of H_2 (the electrostatic contributions cancel in this case). Since the $C_4H^-H_2(j_2 = 0)$ short-range interaction is extremely repulsive for orientations close to linearity ($\theta_1 = 0$ and 180°), there are $N_u = 45$ geometries for which the *ab initio* calculations failed to converge as they correspond to very high interaction energies. In order to get a reliable guess for these missing data points accounting for the known *ab initio* energies at the $N_R \times N_{\theta_1} - N_u = 848$ geometries, we applied the method proposed by Hollebeek, Ho & Rabitz (2001). Then, the expansion coefficients α_{ij} of equation (3) were obtained by solving a set of $N_R \times N_{\theta_1} = 893$ linear equations by means of the Cholesky decomposition method (Golub & Van Loan 1989) and the Tikhonov regularization procedure (Tikhonov & Arsenin 1977). Finally, a fast algorithm via presumptions of the expansion coefficients (Hollebeek, Ho & Rabitz 1997) was implemented to compute the analytical PES. The resulting PES behaves smoothly and produces a root mean square deviation with regards to *ab initio* energies lower than 0.03 cm^{-1} for the 848 geometries (with a maximal deviation lower than 1 cm^{-1}). The analytical PES $V_{av}(R, \theta_1)$ is displayed in Fig. 4 as a contour plot. The global minimum is found for the perpendicular approach of para- $H_2(j_2 = 0)$, at $R = 6.13 \text{ bohr}$ and $\theta_1 = 90^\circ$, with a well depth of -302.54 cm^{-1} .

The strong anisotropy of the $C_4H^-H_2$ interaction at short intermolecular distances can be readily seen in Fig. 4. In order to expand the PES over the convenient set of Legendre polynomials (equation 2), we applied to the analytical PES the regularization procedure of Wernli et al. (2007a). The anisotropy of the PES is

Figure 4. Contour plot of the $C_4H^-H_2$ PES averaged over H_2 orientations as a function of R and θ_1 . Interaction energies are in cm^{-1} .

thus artificially reduced by applying a scaling factor such as the regularized PES tends smoothly to a constant limit value instead of growing high in energy along the repulsive walls. The regularized PES $V_{reg}(R, \theta_1)$ was built from the analytical PES $V_{av}(R, \theta_1)$ as

$$\begin{aligned} V_{reg} &= V_{av} & (V_{av} \leq \epsilon_a) \\ &= \epsilon_a + (\epsilon_b - \epsilon_a) f\left(\frac{V_{av} - \epsilon_a}{\epsilon_b - \epsilon_a}\right) & (\epsilon_a \leq V_{av} \leq \epsilon_b) \\ &= \epsilon_a + (\epsilon_b - \epsilon_a) \left(\frac{2}{\pi}\right)^2 & (V_{av} \geq \epsilon_b) \end{aligned} \quad (4)$$

where the scaling function is given by

$$f(u) = \left(\frac{2}{\pi}\right)^2 \sin\left[\frac{\pi}{2} \sin\left(\frac{\pi u}{2}\right)\right]. \quad (5)$$

We have selected as threshold values $\epsilon_a = 1000 \text{ cm}^{-1}$ and $\epsilon_b = 10000 \text{ cm}^{-1}$, such as the regularized PES coincides with the original one for interaction energies below 1000 cm^{-1} (above the energy domain probed in the present scattering calculations) and tends to a constant value of $\sim 4650 \text{ cm}^{-1}$. The radial expansion coefficients $v_{l_1}(R)$ of equation (2) can be finally obtained at any R value by projecting out the regularized PES $V_{reg}(R, \theta_1)$ on to the basis of Legendre polynomials using a Gauss–Legendre quadrature scheme. Including anisotropic terms up to $l_{1\text{max}} = 60$, we found that the PES resulting from the polynomial expansion is smooth and properly reproduce the regularized PES, with maximal deviations of a few cm^{-1} for interaction energies below 500 cm^{-1} .

3 SCATTERING CALCULATIONS

This study focuses on the following collisional excitation process:

where j_1 and j_2 are the rotational angular momenta of C_4H^- and H_2 , respectively. The energies of the C_4H^- rotational energy levels shown in Table 1 were obtained from the experimental rotational constants of Amano (2008) ($B_0 = 0.1552722 \text{ cm}^{-1}$ and $D_0 = 0.196 \cdot 10^{-7} \text{ cm}^{-1}$). They allow to reproduce within less than 10^{-6} cm^{-1} the observed transition frequencies between the C_4H^- rotational states. The rotational excitation cross-sections corresponding to $j_1 \rightarrow j'_1$ transitions have been determined for rotational levels up to $j_1 = 20$ by means of quantum scattering calculations based on the CC approach of Green (1975). Rotational levels up to $j_1 = 25$ were included into the basis set to obtain converged excitation cross-sections between the 21 first rotational levels.

Figure 5. State-to-state cross-sections for the rotational de-excitation of C_4H^- by para- H_2 ($j_2 = 0$) for selected transitions $\Delta j_1 = j_1 - j'_1 = 1$ as a function of kinetic energy. The cross-sections are labelled according to the related transition $j_1 \rightarrow j'_1$ between the rotational states of C_4H^- .

The CC calculations were performed using the regularized PES $V_{\text{reg}}(R, \theta_1)$ with the quantum scattering code molscat (Hutson & Green 1994). The modified log-derivative Airy propagator of Alexander & Manolopoulos (1987) was employed with a variable step size to solve the CC equations from $R = 3$ to $R = 100$ bohr. The reduced mass of $\text{C}_4\text{H}^- - \text{H}_2$ was taken equal to 1.933 602 amu. Anisotropic terms up to $l_{\text{max}} = 50$ were retained for the PES expansion (equation 2), as it leads to cross-sections which deviate by less than 5 per cent from the results obtained with $l_{\text{max}} = 60$ and avoids prohibitive length calculations. The CC calculations were carried out for total energies ranging from 0.4 to 500 cm^{-1} , with energy grid steps of 0.1 cm^{-1} for $E \leq 110$ cm^{-1} , 0.2 cm^{-1} for $110 \leq E \leq 150$ cm^{-1} , 0.5 cm^{-1} for $150 \leq E \leq 200$ cm^{-1} , 1 cm^{-1} for $200 \leq E \leq 300$ cm^{-1} , and 5 cm^{-1} for $300 \leq E \leq 500$ cm^{-1} . Convergence of the cross-sections required total angular momentum channels up to $J = 126$ to be included at the largest computed energies.

The rotational excitation rate coefficients $k_{j_1 \rightarrow j'_1}(T)$ were obtained for temperatures up to 100 K by averaging the computed cross-sections $\sigma_{j_1 \rightarrow j'_1}(E)$ as

$$k_{j_1 \rightarrow j'_1}(T) = \left(\frac{8k_B T}{\pi \mu} \right)^{\frac{1}{2}} \left(\frac{1}{k_B T} \right)^2 \times \int_0^\infty E_k \sigma_{j_1 \rightarrow j'_1}(E_k) e^{-\frac{E_k}{k_B T}} dE_k, \quad (7)$$

where $E_k = E - \epsilon_{j_1}$ is the relative kinetic energy, μ is the reduced mass of $\text{C}_4\text{H}^- - \text{H}_2$, and k_B is the Boltzmann constant. The rate coefficients for the reverse transitions are given by the detailed balance relation:

$$k_{j'_1 \rightarrow j_1}(T) = \frac{2j_1 + 1}{2j'_1 + 1} \exp\left(\frac{\epsilon_{j'_1} - \epsilon_{j_1}}{k_B T}\right) k_{j_1 \rightarrow j'_1}(T), \quad (8)$$

where ϵ_{j_1} denotes the energy of the rotational level j_1 .

4 RESULTS

4.1 Cross-sections

Cross-sections for the rotational de-excitation of C_4H^- by para- H_2 ($j_2 = 0$) are shown as a function of kinetic energy in Figs 5 and 6 for selected $\Delta j_1 = 1$ and 2 transitions, respectively. As can be seen, the cross-sections exhibit many resonances for kinetic energies below 100 cm^{-1} . This feature relates to the decay of quasi-bound

Figure 6. Same as Fig. 5 for $\Delta j_1 = 2$ transitions.

states formed by the attractive part of the PES. The resonance pattern tends to be washed out for transitions involving high rotational states (see in particular the 15–14 and 15–13 cross-sections in Figs 5 and 6). This is due to the contribution of a large number of coupling terms that give rise to many overlapping resonances. Indeed, the main contribution to a given rotational transition comes from coupling terms $v_{l_1}(R)$ for which $\Delta j_1 \leq l_1 \leq j_1 + j'_1$, with even/odd l_1 values for even/odd Δj_1 (Flower 2007). Accordingly, for transitions associated with a given Δj_1 value, the number of coupling terms involved increases with j_1 . Furthermore, since the magnitudes of the coupling terms tend to diminish with l_1 , the cross-sections values increase rapidly with j_1 for the low j_1 states, and then become almost independent of j_1 for the higher states.

The energy dependence of the cross-sections of Figs 5 and 6 behaves approximately as $E_k^{-1/2}$ with increasing kinetic energy. This is consistent with the behaviour predicted by the Langevin capture model for systems dominated by charge/dipole-induced interactions (Levine 2005). Consequently, we can anticipate a very small temperature dependence for the collisional rate coefficients (since the integral of equation 7 behaves as $T^{3/2}$ in such a case). It is worth to note that a similar energy dependence of the cross-sections was already observed for the rotational de-excitation of C_6H^- by para- H_2 ($j_2 = 0$) and ortho- H_2 ($j_2 = 1$) (Walker et al. 2016). In this case the calculations were based on a rigid-body 4D PES, including both the charge/quadrupole ($\sim R^{-3}$) and charge/dipole-induced ($\sim R^{-4}$) contributions to long-range interactions. Since the two contributions are involved in the scattering by ortho- H_2 , the $E_k^{-1/2}$ energy dependence obtained for both para and ortho species shows that the quadrupole moment of H_2 barely influences the rotational energy transfer for such ion-neutral collisional system.

4.2 Rate coefficients

The rotational de-excitation rate coefficients are displayed as a function of temperature in Figs 7 and 8 for selected $\Delta j_1 = 1$ and 2 transitions, respectively. At the low temperatures considered in this work, the rate coefficients exhibit almost constant values in agreement with the Langevin capture model discussed above. For a given Δj_1 , the rate coefficients values increase rapidly with j_1 for the lowest rotational states, and then become almost independent of the initial rotational state selected, as expected from the trend observed for the cross-sections.

Figure 7. State-to-state rate coefficients for the rotational de-excitation of C_4H^- by para- H_2 ($j_2 = 0$) for selected transitions $\Delta j_1 = 1$ as a function of temperature. The rate coefficients are labelled according to the related transition $j_1 \rightarrow j'_1$ between the rotational states of C_4H^- .

Figure 8. Same as Fig. 7 for selected $\Delta j_1 = 2$ transitions.

The comparison between the C_4H^- and C_6H^- (Walker et al. 2017) rotational de-excitation rate coefficients by para- H_2 ($j_2 = 0$) for $\Delta j_1 = 1, 2$ transitions shows that they behave similarly with temperature and are very close in magnitude, while they are an order of magnitude larger than those obtained for the HC_3N-H_2 system (Faure et al. 2016). Similar results are found from the comparison between the CN^-H_2 and $CO-H_2$ rate coefficients (Kłos & Lique 2011), showing that the rate coefficients for anions cannot be derived from the isolectronic neutral systems.

The de-excitation rate coefficients for rotational transitions out of the initial state $j_1 = 15$ are shown in Fig. 9 at two selected temperatures. Whatever the temperature range, the rate coefficients decrease continuously with increasing Δj_1 , showing a strong propensity in favour of $\Delta j_1 = 1$ transitions. The decrease with Δj_1 is expected from the decreasing magnitude of the coupling terms involved in each transition ($l_1 \geq \Delta j_1$). The decrease is however remarkably slow in the present case, the rate coefficients being lowered by only one order of magnitude going from $\Delta j_1 = 1$ to $\Delta j_1 = 10$. Following Walker et al. (2016), this may be related to the small energy spacings between the C_4H^- rotational levels and the strong anisotropy of the PES in the potential well region that gives rise to efficient couplings between the states. Regarding

Figure 9. State-to-state rate coefficients for the collisional de-excitation of the C_4H^- ($j_1 = 15$) rotational state by para- H_2 ($j_2 = 0$) as a function of $\Delta j_1 = j_1 - j'_1 = 1$ at temperatures $T = 20$ and 100 K.

the PES features, it is worth noticing that the near symmetry of the PES with regards to C_4H^- orientations (see Fig. 4) leads to coupling terms $v_{l_1}(R)$ much larger for even l_1 values than for odd ones in the potential well region. This is no more true in the long-range part of the interaction, where the coupling terms are much weaker and decrease continuously with l_1 irrespective of the parity. According to the semi-classical model of McCurdy & Miller (1977), if the rotational energy transfers were governed by short-range interactions we should have observed a clear propensity rule in favour of even Δj_1 transitions. Instead, the results of Fig. 9, and the qualitative agreement with the Langevin capture model, suggest that the collision-induced energy transfers are mainly driven by long-range interactions. Similar results were obtained for other anionic systems in collision with H_2 , C_6H^- (Walker et al. 2017), and CN^- (Kłos & Lique 2011). Since in both cases the rate coefficients for para- H_2 and ortho- H_2 species were found almost similar, we believe that the present set of rate coefficients for C_4H^- /para- H_2 could be employed as a first guess for the C_4H^- /ortho- H_2 rate coefficients.

The complete sets of rotational (de-)excitation rate coefficients will be made available through the LAMDA (Schöier et al. 2005) and BASECOL (Dubernet et al. 2013) data bases.

5 SUMMARY AND CONCLUSION

The rotational excitation of C_4H^- by para- H_2 is addressed for the first time in this study. Full quantum CC scattering calculations of cross-sections and rate coefficients were performed based on a 2D PES suitable to describe the collisional excitation by para- H_2 ($j_2 = 0$). The 2D PES was built as an average of the 4D $C_4H^-H_2$ PES over orientations of the H_2 molecule. The $C_4H^-H_2$ *ab initio* PES was computed for five selected orientations of H_2 at the CCSD(T) level of theory, using aVTZ and aVQZ atomic basis sets to describe C_4H^- and H_2 , respectively. Owing to the strong anisotropy of the 2D PES with regards to C_4H^- orientations at short-range, a fitting procedure based on the RKHS method was employed. The resulting PES was then projected on to a convenient basis of Legendre polynomials to determine the coupling terms involved in scattering calculations.

The rotational excitation rate coefficients have been computed for the first 21 rotational levels of C_4H^- and for temperatures up to

100 K. The state-to-state rate coefficients display almost constant values over the entire range of temperature considered, in agreement with the predictions of the Langevin capture model. Whatever the temperature range, the rate coefficients exhibit propensity rules in favour of $\Delta j_1 = 1$ rotational transitions, and a remarkable slow decrease of their magnitudes with increasing Δj_1 is found. Similar features were observed for the rotational excitation of the C_6H^- (Walker et al. 2017) and CN^- (Kłos & Lique 2011) anionic species by H_2 . The present set of rate coefficients can serve the modelling of C_4H^- emission lines in astrophysical environments.

Future work will concern calculations of C_4H^- in collision with both para- and ortho- H_2 species using a 4D PES approach in order to obtain rate coefficients for highly excited rotational states and higher temperatures. Detailed comparison with other systems, in particular carbon chain anions, will be studied in details owing to its great interest for astrophysical modelling.

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APPENDIX

The $\text{C}_4\text{H}^- - \text{H}_2$ PES employed in this work has been obtained from *ab initio* calculations performed at the CCSD(T) level of theory, using aVTZ and aVQZ atomic basis sets to describe the C_4H^- and H_2 species, respectively. In order to check the

Figure A1. $C_4H^-H_2$ interaction potential as a function of R for two selected orientations $(\theta_1, \theta_2, \Phi)$ of the fragments obtained from different sets of *ab initio* calculations (see text for details).

accuracy of our CCSD(T)/aVQZ/aVTZ approach, we performed for selected geometries CCSD(T) calculations using aVQZ basis sets for all atoms, as well as explicitly correlated coupled-cluster calculations (CCSD(T)-F12A) (Knizia, Adler & Werner 2009) using aVTZ basis sets for all atoms. The CCSD(T)-F12A approach is expected to give results fairly close to the CCSD(T) complete basis set (CBS) limit, with a computational cost reduced by large factors. For the $C_4H^-H_2$ system, the CCSD(T)-F12A/aVTZ energy at the PES minimum was found to be -799.54 cm^{-1} , closer to the CCSD(T)/aVQZ value (-791.15 cm^{-1}) than our CCSD(T)/aVQZ/aVTZ result (-780.27 cm^{-1}). However, as it is actually implemented in molpro (Werner et al. 2012), the F12 treatment of the triples energy correction is not explicitly calculated, but taken into account applying a scaling term to the triples energy. Such a procedure can break the size consistency of the CCSD(T) approach (Knizia et al. 2009), giving rise to a non-zero decay of the interaction potential at large intermolecular distances. For the present system, the CCSD(T)-F12A/aVTZ interaction energy at $R = 100 \text{ bohr}$ is -7 cm^{-1} for all orientations, while the CCSD(T)/aVQZ/aVTZ and CCSD(T)/aVQZ approaches provide a negligible value, as expected. The simplest way to overcome this problem is to shift the whole PES by the interaction energy value obtained at large R (see for example Sahnoun et al. 2017).

We display in Fig. A1 the R -dependence of the $C_4H^-H_2$ interaction potential obtained from the three sets of *ab initio*

calculations (plus the result of the shifting procedure) for two selected orientations of the fragments. The first one, $(\theta_1, \theta_2, \Phi) = (0, 0, 0)$, corresponds to the global minimum of the 4D PES (see Fig. 2). The second one, $(\theta_1, \theta_2, \Phi) = (\pi/2, \pi/2, 0)$, corresponds to a saddle-point of the 4D PES (see in Fig. 3) which relates to the global minimum of the 2D PES (Fig. 4). As can be seen in Fig. A1, for the collinear orientation of the fragments (0,0,0), the shifted CCSD(T)-F12A/aVTZ results are in close agreement with the CCSD(T)/aVQZ ones whatever the range of intermolecular distances. This is not the case for the H orientation of the fragments $(\pi/2, \pi/2, 0)$, where the shifted CCSD(T)-F12A/aVTZ results lead to underestimate the $C_4H^-H_2$ interaction at intermediate and long-range intermolecular distances. By contrast, the CCSD(T)/aVQZ/aVTZ approach provides a correct description of long-range interactions, and is of similar accuracy compared to the shifted CCSD(T)-F12A/aVTZ results at short range. We found a similar behaviour for several other orientations of the fragments. Since the long-range interactions are of crucial importance for the present collisional excitation process, we chose to use the CCSD(T)/aVQZ/aVTZ results instead of the shifted CCSD(T)-F12A/aVTZ ones to describe the $C_4H^-H_2$ PES.

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