Interaction of CH₃CN and CH₃NC with He : potential energy surfaces and low-energy scattering

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Several nitrogen-bearing molecules, such as methyl cyanide (or acetonitrile, CH₃CN) and methyl isocyanide (CH_3NC) of interest here, have been observed in various astrophysical environments. The accurate modeling of their abundance requires the calculation of rate coefficients for their collisional excitation with species such as He atoms or H_2 molecules at low temperatures. In this work we compute new three-dimensional potential energy surfaces for the CH_3NC -He and CH_3CN -He van der Waals complexes by means of the explicitly correlated coupled cluster approach with single, double and perturbative triple excitation CCSD(T)/F12a in conjunction with the aug-cc-pVTZ basis set. We find a global minimum with $D_e = 55.10$ and 58.61 cm^{-1} for CH_3CN -He and CH_3NC -He, respectively, while the dissociation energy D_0 of the complexes are 18.64 and 18.65 cm^{-1} , respectively. Low energy scattering calculations of pure rotational (de-)excitation of CH₃CN and CH_3NC by collision with He atoms are carried out with the close-coupling method and the collisional cross sections of ortho- and $para-CH_3NC$ and CH_3CN are computed for kinetic energies up to 100 cm⁻¹. While the PESs for both complexes are qualitatively similar, that of CH_3NC -He is more anisotropic, leading to different propensity rules for rotational excitation. For CH₃NC-He, we find that $|\Delta i| = 1$ transitions are dominant at low kinetic energy and a propensity rule that favors odd Δj transitions is observed, whereas for CH₃CN the dominant cross sections are associated to transitions with $|\Delta j| = 2$. We expect that the findings of this study will be beneficial for astrophysical investigations as well as laboratory experiments.

I. INTRODUCTION

Methyl cyanide (or acetonitrile, CH_3CN) is one of the most ubiquitous interstellar organic molecules. It has been detected in a variety of low- and high-mass sources^{1,2}. Thanks to its three-fold symmetry and its large dipole moment, CH_3CN is often used as a gas thermometer to probe interstellar environments and it is a useful tracer of dense gas^{3,4}. Its isomer CH_3NC is thermodynamically the less stable isomer of CH_3CN . CH_3NC was tentatively observed for the first time in 1988 in the Sgr B2 cloud⁵ and confirmed with additional rotational transitions seventeen years later by Remijan et al. ⁶ Since then, it has been observed only in a handful of sources⁷, including the Horsehead nebula photodissociation region (PDR)⁸, as well as Orion KL⁹.

For typical dense cloud conditions, theoretical calculations by DeFrees et al.¹⁰ estimated the ratio of CH₃NC/CH₃CN to be in the range of 0.1 - 0.4. However, Cernicharo et al.⁵ deduced from their observations an abundance ratio of ~ 0.03 - 0.05, showing that the relative abundance of CH₃CN is larger than previous estimates. Later, Gratier et al.⁸ found, according to their observations in the Horsehead region, an abundance ratio CH₃NC/CH₃CN in agreement with estimations of Defrees. Therefore, it appears that accurately determining the abundances of CH₃CN and CH₃NC may provide clues to understand their respective chemistry in space, and the formation and evolution of interstellar clouds can be explored through isomer comparison studies.

Acetonitrile and methyl isocyanide are symmetric top molecules that display close similarities in their molecular parameters such as the bond length^{11,12} and electric dipole moment¹³, which cannot introduce any bias in their respective rotational spectra. Unfortunately, the abundance of CH₃NC is not well constrained as its abundance is estimated using excitation rate coefficients of CH₃CN, an approximation that might not be valid. In order to satisfy astrophysical precision when modelling the abundance of interstellar species, we need calculations of rate coefficients for rotational excitation induced by collision with the most abundant species (H₂, He, and H).

In the present paper, we study the collision of the rigid symmetric top molecules CH₃CN and CH₃NC with He at low collision energies $(E_{coll} \leq 100 \text{ cm}^{-1})$, with the aim of understanding their excitation and the impact of isomerization on the rotational excitation. A PES for CH₃CN-He has been reported recently¹⁴ and used to investigate the rotational excitation of CH₃CN. However, due to an error in the angular expansion of the potential, the radial coefficients used for the scattering computations were not correct. As a consequence, the CH₃CN-He cross sections were impacted by an error that can reach an order of magnitude for some transitions, making a meaningful comparison with CH₃NC-He cross sections impossible. Consequently, in order to establish a detailed comparison between the interaction and collisional excitation properties of methyl cyanide and methyl isocyanide with helium atoms, we compute new PESs for both isomers at exactly the same computational level and basis set.

Finally, we note that the reactivity of methyl cyanide with molecular ions at low temperature has been studied experimentally by several groups¹⁵⁻¹⁷. Ideally, this requires molecules that are cooled prior to the reaction. Several approaches to produce cold beams of CH_3CN have been reported^{15,18,19}, which allow the production of CH_3CN in the ground rotational state²⁰. Another possibility would be to use a Stark decelerator. Cooling can also be achieved by loading the CH_3CN molecules into a helium buffer gas cell, and the knowledge of the rotational excitation cross sections and rate coefficients can be used to model the dynamics in the cell^{21,22}.

The overall structure of this paper is as follows: first, we present in Section II an *ab initio* study of the CH₃CN/NC-He systems, leading to new 3D-PESs corresponding to the interaction between CH₃CN/NC and He. Section III is dedicated to the investigation of the dissociation energy of the complexes, while in Section IV we describe the study of the dynamics of the collision, restricted in the present article to the low-energy regime, which we illustrate with inelastic cross sections in CH₃CN-He and CH₃NC-He collisions. Conclusions and future outlooks are drawn in Section V.

II. POTENTIAL ENERGY SURFACES

A. Ab initio calculations

We focus here on the interaction between a symmetric top molecule, CH_3NC or its isomer CH_3CN , with a structureless helium atom (¹S) in their respective electronic ground states. In the present work, we consider these molecules to be rigid rotors, leading to a threedimensional potential energy surface (3D-PES). Since both CH_3CN and CH_3NC possess a low energy vibrational bending mode (365 and 270 cm⁻¹, respectively), we note that the PES should eventually include a dependence on this vibrational coordinate to treat collisional excitation except at low temperatures.

The coordinate system used in this work is presented in Figure 1. The origins of the reference frames are the centers of mass of CH₃NC and CH₃CN respectively and the C_3 principal axis of CH₃ is located along the z axis. Consequently, three degrees of freedom are needed to describe the interaction potential of CH₃NC-He and CH₃CN-He. We use the following coordinates: (i) the distance R between the center of mass of the target systems to the helium atom, (ii) the polar angle θ , which describes the position of the helium atom with respect to the z-axis, and (iii) the azimuthal angle ϕ that describes the rotation of the He atoms around the z axis.

The 3D-PESs are calculated within the rigid rotor approximation and the internal coordinates of methyl (iso)cyanide are described using the experimental ground vibrational geometries as follows: $r(N\equiv C)=1.167\text{\AA}$, $r(C-N)=1.416\text{\AA}$, $r(C-H)=1.093\text{\AA}$, and $\angle(HCH)=109.5^{\circ}$ for CH₃NC²³ and $r(C\equiv N)=1.156\text{\AA}$, $r(C-C)=1.457\text{\AA}$, $r(C-H)=1.087\text{\AA}$, and $\angle(HCC)=110^{\circ}$ for CH₃CN²⁴. Consequently, the PESs were computed using 52 values of R ranging from 3.75 to 50a₀, 19 values of θ uniformly span-



FIG. 1. Jacobi coordinates used to describe the interaction of CH₃NC-He van der Waals complex. The origin of the reference frame is at the CH₃NC center-of-mass. The angles are defined so that for $\theta = 0^{\circ}$ He approaches along the NC/CN end of the molecule and for $\phi = 0^{\circ}$ the He atom lies in the plane defined by (NC/CN)CH atoms on the side of the H atom.

ning the range $[0^{\circ}-180^{\circ}]$ by steps of 10° and 7 values of ϕ angles in the range $[0-60^{\circ}]$. These parameters lead to a set of 6916 energy points.

The *ab initio* energies were computed using the MOL-PRO package²⁵ and treated in the C₁ symmetry group. We use the explicitly correlated coupled cluster method with inclusion of single, double and non-iterative triple excitations [CCSD(T)-F12a]²⁶ in conjunction with the augmented correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) basis sets of Dunning²⁷. The CCSD(T)-F12a method with the aug-cc-pVTZ basis set should lead to an accurate PES. Indeed, it has been shown that CCSD(T)-F12 with AVnZ basis sets yields an accuracy comparable to standard CCSD(T) with AV(n+1)Z basis sets with reduced computational time²⁶.

We take into account the correction for the basis set superposition errors (BSSE) using the counterpoise procedure of Boys and Bernardi²⁸ according to the following expression:

$$V(R,\theta,\phi) = V_{\text{Mol-He}}(R,\theta,\phi) - V_{\text{Mol}}(R,\theta,\phi) - V_{\text{He}}(R,\theta,\phi)$$
(1)

where $V_{\text{Mol-He}}$ is the global electronic energy of CH₃NC-He and CH₃CN-He systems, and the last two terms are the energies of the two fragments, all performed using the full basis set of the total system.

A disadvantage of the CCSDT(T)-F12a method is that it is not size consistent, therefore, the PESs computed with this approach were shifted by subtracting the asymptotic value of the interaction potential, which is equal to -4.09 cm^{-1} for CH₃NC-He and -4.80 cm^{-1} for CH₃CN-He.

B. Analytical fit

As required by MOLSCAT²⁹ and HIBRIDON³⁰ codes that were used for the scattering calculations, we fitted our *ab initio* data to an analytical expansion in order to produce the global PES $V(R, \theta, \phi)$ according to the following functional form³¹:

$$V(R,\theta,\phi) = \sum_{l=0}^{l_{max}} \sum_{m=0}^{l} V_{lm}(R) Y_l^m(\theta,\phi)$$
(2)

Taking into consideration the property of spherical harmonics, the 3D-PESs can be written as:

$$V(R,\theta,\phi) = \sum_{l=0}^{l_{max}} \sum_{m=0}^{l} V_{lm}(R) \frac{Y_l^m(\theta,\phi) + (-1)^m Y_l^{-m}(\theta,\phi)}{1 + \delta_{m,0}}$$
(3)

where $V_{lm}(R)$ and $Y_l^m(\theta, \phi)$ denote the radial coefficients to be computed and the normalized spherical harmonics respectively, and $\delta_{m,0}$ is the Kronecker symbol.

Due to the C_{3v} symmetry of the CH₃NC molecule and its isomer, the parity of the expansions is constrained to m multiple of 3 (m = 3n, n integer). Hence, as we used 19 values of θ and 7 values of ϕ angles to compute the *ab initio* PESs, we can compute radial coefficients up to $(l_{max}, m_{max}) = (18, 18)$, leading to a set of 70 angular functions. Scattering calculations require continuous radial coefficients, and for each value of R we used a least-square procedure to generate the $V_{lm}(R)$ radial coefficients. This development reproduces the global ab initio potential with a root means square deviation (rms) of 1.0 cm^{-1} . The rms is much larger in the short range due to the larger anisotropy of the PES, e.g., at $R = 4.75a_0$ it is equal to 224 cm⁻¹. The rms becomes less than 1 cm⁻¹ for distances $R \ge 6a_0$ and decreases with increasing R, which shows that the minimum of the PES and the long-range region are adequately described. For $R \geq 30$ bohr, we extrapolated the long-range potential using an inverse exponent expansion implemented in the MOLSCAT code. We illustrate in figure 2 the dependence on R of the radial coefficients up to l = 4 for CH₃NC and CH_3CN . Here, V_{00} represents the isotropic potential, responsible for elastic collisions, while terms with $l \geq 1$ describe the anisotropic part of the PES responsible for inelastic collisions. As a first outcome of the fitting, we note that the isotropic term V_{00} presents a deeper well for CH₃CN-He (65.8 cm⁻¹) than CH₃NC-He (56.2 cm⁻¹). In addition, we note that for a given distance, the V_{lm} with even values of l are larger for CH₃CN than those for CH₃NC and V_{lm} with odd value of l are deeper for CH_3NC compared to those for CH_3CN . This is expected to have an effect on the propensity rules in the rotational excitation, as shall be further discussed below.



FIG. 2. Dependence on R of the first $V_{lm}(R)$ components for CH₃CN-He (solid lines) and CH₃NC-He (dashed lines) with $0 \le l \le 4$.

C. Analysis of the PES

For CH₃NC-He, a global minimum with $D_e = 58.61$ cm⁻¹ exists at $\phi = 60^{\circ}$, $\theta = 100^{\circ}$ and R = 6.05 bohr while a local minimum of 46.77 cm⁻¹ is located at $\theta = 180^{\circ}$ and R = 8.5 bohr.

For CH₃CN-He, the PES present a global minimum with a depth of $D_e = 55.10 \text{ cm}^{-1}$ for the configuration $\phi = 60^{\circ}$, $\theta = 100^{\circ}$ and R = 6.15 bohr while the local minimum of 38.47 cm⁻¹ is located at R = 8.6 bohr and $\theta = 180^{\circ}$. We note that the PESs for these isomers share the same qualitative behavior previously observed for molecules with a threefold symmetry axis interacting with rare gas atoms^{32–34} where the global minimum occurs at $\phi = 60^{\circ}$, *i.e.* with the helium atom located between two hydrogen atoms. However, the global minimum as well as the local minimum of CH₃NC-He are deeper than those of CH₃CN-He.

The global and local minima are separated by a transition state of -29.05 cm^{-1} located at $\theta=139.5^{\circ}$ and R=8.25 bohr for CH₃NC-He, while for CH₃CN-He this transition state is at R=8.5 bohr and $\theta=143^{\circ}$ with an energy of -28.51 cm^{-1} .

We illustrate in Fig 3 two-dimensional cuts of the interaction potentials as a function of two Jacobi coordinates, while the third one is held fixed at its equilibrium values in the CH₃NC-He and CH₃CN-He minimum. The variation in those cuts shows a stronger anisotropy of the interaction potential of CH₃NC-He compared to CH₃CN-He along the θ coordinate.

We compared the new 3D-PES of CH_3CN -He with the earlier CH_3CN -He PES computed using the automated

interpolating moving least squares methodology¹⁴. We conclude that the two PESs are qualitatively and quantitatively similar, the energies and locations of the stationary states being almost identical. As an example, the global minimum was found at ϕ =60°, θ =100.4° and R=6.14 bohr with an energy of 55.16 cm⁻¹, to be compared to our values of 55.10 cm⁻¹ at ϕ =60°, θ = 100.0° and R=6.15 bohr.

For a better appreciation of the topography of the PESs, we present also 2D-cut of the 3D-PESs as a function of θ and ϕ for R = 6.1 bohr in the bottom panels of Fig. 3. This type of plot offers a unique overview as it includes all minima and the barriers between them. Its should also be noted that the potential for CH₃NC-He is much more repulsive than that of CH₃NC-He at small and large values of θ , while the two PESs are similar in the region of the minimum. This leads to a higher anisotropy for the CH₃NC-He potential, as already alluded to above.

III. BOUND STATES

We have computed the energies of bound vibrational levels of the CH₃CN–He and CH₃NC–He van der Waals complexes in order to determine the dissociation energy D_0 of the complexes. A set of basis functions formed from the product of stretching and body-fxed angular functions was employed³¹. The *R*-space was spanned by a set of 16 distributed Gaussians³⁵. The width of the Gaussians is 1.33 a_0 and the range is spanned from 5 to 11 a_0 . The HIBRIDON code³⁰ was employed to determine the energies of the bound vibrational levels.

Due to the permutation of the three hydrogen atoms, the rotational levels of CH₃NC and CH₃CN are divided into two groups: $A-CH_3NC/CN$ (ortho) and E-CH₃NC/CN (para) corresponding to the A_1 or A_2 , and E irreducible representations of the C_{3v} point group. In fact, each hydrogen nucleus possesses a nuclear spin 1/2, hence, if we couple the three hydrogen nuclear spins, we obtain a total nuclear spin equal to I=3/2(ortho-CH₃NC/CN) or I=1/2 (para-CH₃NC/CN). The rotational states of para-CH₃NC/CN correspond to $k=3n \pm 1$, while those of ortho-CH₃NC/CN correspond to k=3n for (n being integer).

Separate calculations of the dissociation energies of van der Waals complexes of the ortho and para levels of CH₃CN–He and CH₃NC–He were carried out. The dissociation energy D_0 of ortho-CH₃CN–He and ortho-CH₃NC–He complexes were found to almost equal: $D_0(ortho-CH_3CN-He) = 18.64 \text{ cm}^{-1}$ and $D_0(ortho-CH_3NC-He) = 18.65 \text{ cm}^{-1}$. Levels up to j = 24 were required in the rotational basis set for convergence of the dissociation energy. No bound levels were found for the para-CH₃CN–He and para-CH₃NC–He complexes. The dissociation energies are summarized in Table I.

TABLE I. Dissociation energies D_0 (in cm⁻¹) of the *ortho* and *para* levels of CH₃CN–He and CH₃NC–He

	CH ₃ CN-He	CH ₃ NC-He
or tho	18.64	18.65
para	0	0

IV. SCATTERING CALCULATIONS

A. Spectroscopy of CH₃CN and CH₃NC

 CH_3CN and CH_3NC are prolate symmetric top molecules. The relevant Hamiltonian of such a symmetric rotor is given by:

$$H_{rot} = \frac{\hbar^2}{2I_b} j^2 + \hbar^2 (\frac{1}{2I_a} - \frac{1}{2I_b}) j_a^2 \tag{4}$$

where j is a rotational quantum number that satisfies the relation $j^2 = j_a^2 + j_b^2 + j_c^2$ and I_a and I_b are the principal moments of inertia. The rotational wave functions $|jkm\rangle$ of both isomers are defined by three quantum numbers, where k denotes the projection of j along the a-axis of the body-fixed reference and m is its projection on the z-axis of the space-fixed frame of reference. The eigenvalues is the energies of the rotational levels, given by :

$$E_{j,k} = Bj(j+1) + (A-B)k^2$$
(5)

where B and A are the rotational constants which are equal to 0.3353 cm⁻¹ and 5.2420 cm⁻¹ for CH₃NC³⁶ and 0.3068 cm⁻¹ and 5.2470 cm⁻¹ for CH₃CN³⁷ respectively.

For illustration, we present in figure 4 the rotational energy diagram associated to the CH₃NC and CH₃CN levels up to j = 9. It must be emphasized that the *ortho*- and *para*- states cannot be interconverted either by radiative transitions, nor by inelastic collisions: hence, the conversion from *ortho*-CH₃NC/CN to *para*-CH₃NC/CN is forbidden (and vice versa) and the scattering calculations can be performed separately for each nuclear spin species.

The small value of the rotational constant B leads to a high density of rotational levels even at low energy. In astrophysical environments, CH₃CN and CH₃NC are indeed often observed through transitions involving highly excited states, e.g. 17_k to 16_k , k=0,...,7 and 18_k to 17_k , k=0,...,7) for CH₃NC⁷. This implies that the theoretical study of rotational excitation of methyl (iso)cyanide requires a large basis set of rotational levels, which in turn limit the possibility of using fully quantum-mechanical dynamics methods to low collision energies.

B. Cross section computations

In this work, we present cross sections for rotationally inelastic transitions up to $E_{tot} \leq 100 \text{ cm}^{-1}$, computed using the time-independent close-coupling (CC)



FIG. 3. Two-dimensional contour plots of the interaction potential of the CH₃CN-He (left panels) and CH₃NC-He (right panels) van der Waals complex. Top panels depict the 3D-PESs as a function of θ and R at $\phi = 60^{\circ}$, while the bottom panels show the PESs as a function of ϕ and θ at R = 6.1 a₀. For each panel, the blue (red) contours represent the positive (negative) parts of the potential (in unit of cm⁻¹).

method. In order to perform the scattering calculations of CH₃NC-He and CH₃CN-He colliding systems, we introduced radial coefficients $V_{lm}(R)$ in MOLSCAT code using the VSTAR routine. The diabatic logderivative propagator is used in order to solve the coupled equations³⁸. Some of the calculations were carried out with the HIBRIDON suite of programs³⁰. We do not take into consideration the hyperfine excitation in both isomers because the component splitting is not yet resolved by the astrophysical observations. We focus here on the low energy $(E \leq 100 \text{ cm}^{-1})$ scattering of CH₃NC-He and CH₃CN-He. In order to properly converge collisional cross sections, preliminary tests were performed in order to find the optimal parameters at several energies. This includes the integration boundaries of the propagator, R_{min} and R_{max} , which were fixed at 2.5 and 50 bohr respectively; the number of integration steps, taken as 100 for $E_{tot} \leq 50 \text{ cm}^{-1}$ and 70 for $E_{tot} \in [50,100] \text{ cm}^{-1}$; as well as the size of the rotational basis set which includes all open channels and some closed



FIG. 4. Rotational levels of para- and $ortho-CH_3NC$ (circles) and CH_3CN (diamonds) up to $j_k = 9_9$.

channels. Rather than including all rotational states up to a given j_{max} , it is more convenient to use a cutoff based on energy and include all states up to that value. For $ortho-\text{CH}_3\text{NC}$, it was found necessary to include the 35 lowest levels (up to $j_k = 20_0$ with an energy of 140.8 cm⁻¹) for total energies $E_{tot} \leq 50 \text{ cm}^{-1}$ and 55 levels (up to $j_k = 26_0$ with an energy of 235.4 cm⁻¹) for 50 $\leq E_{tot} \leq 100 \text{ cm}^{-1}$, while for $ortho-\text{CH}_3\text{CN}$ we need the first 55 (up to $j_k = 29_3$, energy of 225.6 cm⁻¹) and 65 levels (up to $j_k = 29_3$, energy of 311.4 cm⁻¹), respectively. For $para-\text{CH}_3\text{NC}$ -He, the first 65 rotational levels (up to $j_k = 13_5$, with an energy of 183.7 cm⁻¹) are necessary to converge cross sections for $E_{tot} \leq 50 \text{ cm}^{-1}$, and 75 states (up to $j_k = 20_4$ with an energy of 219.3 cm⁻¹) for $E_{tot} \in [50,100] \text{ cm}^{-1}$, while for $para-\text{CH}_3\text{CN}$, we take the first 78 rotational levels (up to $j = 18_7$, with an energy 346.9 cm⁻¹) for $E_{tot} \leq 100 \text{ cm}^{-1}$.

The energy grid was chosen as dense enough to describe resonances at the various thresholds corresponding to the opening of rotational levels, and the spacing is significantly increased outside the resonance zones. For $0 < E_{tot} \leq 50 \text{ cm}^{-1}$ we used a step size of 0.2 cm^{-1} , while for $50 < E_{tot} \leq 100 \text{ cm}^{-1}$ the step size was 0.5 cm^{-1} . The reduced mass is taken at $\mu = 3.646815237$ atomic mass unit (isotopes ${}^{12}\text{C}, {}^{14}\text{N}, {}^{1}\text{H}$ and ${}^{4}\text{He}$).

Figures 5 and 6 present the plots of collisional excitation cross sections of $para-CH_3NC/CN$ -He and $ortho-CH_3NC/CN$ -He, as a function of the kinetic energy for transitions from the ground state, namely 0_0 for ortho species and 1_1 for para species to levels j_k (Panels a and b), and for dipolar ($\Delta j = 1$) and quadripolar ($\Delta j = 2$) transitions with k = 0, 1, 2, 3 (Panels c,d,e and f). We note the presence of both Feshbach and shape resonances for kinetic energies below 60 cm⁻¹. Such features are expected, since the global minima of the PESs of the CH₃NC-He and CH₃CN-He complexes are found to be slightly less than 60 cm^{-1} . These resonances arise from the tunnelling of the projectile through the centrifugal energy barrier (shape resonances) or to a temporary trapping of the projectile by the potential leads to CH₃NC-He and CH₃CN-He complexes quasi-bound states (Feshbach resonances). The character of the individual resonances can be analysed by inspecting the wave functions³⁹. The resonances disappear and the cross sections becomes smooth and continue to decrease for energies $E_{tot} \ge 60 \text{ cm}^{-1}$. Comparing the cross sections for CH₃NC-He (left panels) and CH₃CN-He (right panels), we can see that the relative order of magnitudes of the CH_3NC -He cross sections are larger than those for CH_3CN -He, which can be explained by the larger well depth of the CH₃NC-He PES compared to that of the CH_3CN -He PES.

In addition, we note also significant differences between the CH₃CN-He and CH₃NC-He cross sections. Figures 5 and 6 reveal the existence of a strong even Δi propensity rule for almost all energies for CH₃CN-He. The largest cross sections are found for the quadripolar transitions $0_0 - 2_0$, $1_0 - 3_0$ and $2_0 - 4_0$ for $ortho-CH_3CN$ -He and for the transitions $1_1 - 3_1$, $2_1 - 4_1$ and $3_1 - 5_1$ for para-CH₃CN-He. On the other hand, for its isomer CH₃NC-He, the predominance of cross sections is associated to transitions with $|\Delta j| = 1$ for $E_c \leq 40 \text{ cm}^{-1}$. It should be noted that this propensity rule changes with increasing energy, and transitions $|\Delta j| = 2$ become favored for $E_c \geq 40 \text{ cm}^{-1}$. The propensity rules of the collisional cross sections can be understood by examining the shape of the PES : the higher symmetry of the CH₃CN-He PES will favour transitions with even $|\Delta j|$ whereas the anisotropic PES of CH₃NC-He favors transitions with odd $|\Delta j|^{40}$. In addition, this propensity rule can be explained by interpreting the expansion coefficients $V_{lm}(R)$ presented in figure 2. For example, inelastic cross sections involving $|\Delta j| = 1$ are caused by the V_{10} term, which is the dominant term for CH₃NC-He, so that the cross section corresponding to the 1_0 - 0_0 transition is larger than for other transitions. However, for CH₃CN-He, the dominant term is V_{20} , a term responsible for transitions involving $|\Delta j| = 2$, hence, the largest cross sections are obtained for even Δj transitions. Such results were already observed for other systems : propensity rules which favor $|\Delta j| = 2$ were also found for X-CN systems such as SiH₃CN⁴¹, HCN⁴², CCN⁴³ and which favor $|\Delta j| = 1$ for X-NC complex such as HMgNC⁴⁴, HNC⁴², NaNC⁴⁵ as well as MgNC and AlNC⁴⁶. Recently, collisions of HCN-He and HNC-He were investigated experimentally with chirped pulse in uniform supersonic flow technique by Hays et al.⁴⁷. Good agreement between the scattering calculations and experimental measurements was found, and similar effects of propensity rules were observed for collisions of HCN and HNC with He atoms.

Finally, we note that for *para* states collisional cross sections for transitions with $|\Delta j| = 1$ and $|\Delta k| = 0$ are strongly dominant over transitions associated with

 $|\Delta j|=1$ and $|\Delta k| = 1$ (not shown). In addition, resonances almost do not exist for cross sections involving levels with $|\Delta k| = 1$, due to the large threshold energy value.

It should be noted that no rate coefficients for CH₃NC excitation by collision with helium are available in the literature, and the interpretation of astrophysical observation is usually realised by using the CH₃CN-He collisional rates, since the dipole moment of CH₃NC and its isomers are almost identical (μ =3.92 D for CH₃CN and $\mu=3.89$ D for CH₃NC) and the energies of the rotational levels are almost equal. However, the comparison of the corresponding cross sections of both isomers displays large differences that will be reflected on the magnitude of collisional rate coefficients. We conclude that the use of CH₃CN rate coefficients in the interpretation of CH₃NC observations may be dangerous for the astrophysical applications, since the use of CH₃CN collisional rate coefficients will probably significantly modify the excitation of the CH₃NC molecule. This will be explored in future research.

V. CONCLUSIONS

In this paper, we have calculated accurate, state-ofthe-art 3D-PESs corresponding to the interaction of rigid CH₃CN and CH₃NC molecules with an He atom using the CCSD(T)-F12a/aug-cc-pVTZ level of theory to study the rotational excitation induced by molecule-atom collisions. The potential well depths are moderate, with a global minimum of about 58 cm⁻¹ for CH₃NC-He and 55 cm⁻¹ for CH₃CN-He, allowing a high quality study of the dynamics. Using these PESs, we have computed cross sections for total energies ranging from the threshold up to 100 cm⁻¹ for both isomers. Our calculations show the dominance of $|\Delta j| = 1$ transitions for CH₃NC-He collisions and a dominance of $|\Delta j| = 2$ transitions for CH₃CN excitation by He atoms.

CH₃CN is one of the most ubiquitous detected molecule in astrophysical clouds, where it acts as practical gas thermometers of the interstellar cloud. Its isomer CH₃NC is the less stable isomer of CH₃CN, and astrophysicists have often used CH₃CN in order to understand the abundance of interstellar CH₃NC. As demonstrated in this paper, cross sections computed based on an appropriate PESs and with quantum-mechanical techniques are very different between both isomers. We thus expect this to impact significantly the abundance of the CH₃NC isomer, when non-local thermodynamic equilibrium conditions prevail. The high energy scattering as well as the corresponding rate coefficients and their impact on the interpretation of observations of methyl (iso)-cyanide will be published in a forthcoming paper.

ACKNOWLEDGMENTS

J.L. acknowledges support from KU Leuven through Grant No. 19-00313.

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FIG. 5. Kinetic energy dependence of the rotational excitation cross sections $j_k \rightarrow j'_{k'}$ of $para-CH_3NC$ -He (left panels) and $para-CH_3CN$ -He (right panels) in collision with He. (a), (b): transitions from the ground rotational state (1₁) to various j'_k ; (c), (d): comparison of $\Delta j = 1$ and $\Delta j = 2$ transitions while k = k' = 1; (e), (f): comparison of $\Delta j = 1$ and $\Delta j = 2$ transitions while k = k' = 2.





FIG. 6. Kinetic energy dependence of the rotational excitation cross sections $j_k \rightarrow j'_{k'}$ of $ortho-CH_3NC$ -He (left panels) and $para-CH_3CN$ -He (right panels) in collision with He. (a), (b): transitions from the ground rotational state (0₀) to various j'_k ; (c), (d): comparison of $\Delta j = 1$ and $\Delta j = 2$ transitions while k = k' = 0; (e), (f): comparison of $\Delta j = 1$ and $\Delta j = 2$ transitions while k = k' = 3.

