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## EXPERIMENTAL AND THEORETICAL ANALYSIS OF LOW-ENERGY CO + H<sub>2</sub> INELASTIC COLLISIONS

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### ABSTRACT

Carbon monoxide is one of the most abundant components in many interstellar media and modeling its spectra requires knowledge of rate coefficients for the rotational (de-)excitation by collision with the dominant species in molecular regions, H<sub>2</sub>. In this Letter, we report on experimental observation of resonances in the collisional excitation of CO by *para*- and *ortho*-H<sub>2</sub> at low collision energies characteristic of cold molecular clouds (down to a few Kelvin). Our experimental integral cross sections are compared to the results of new quantum mechanical scattering calculations performed using the highly accurate ab initio potential energy surface of Jankowski et al. Since the scattering calculations are very sensitive to the accuracy of the potential, especially when quantum resonances are involved, the quality of the agreement between theory and experiment reinforces the confidence in the observables derived from this potential energy surface, such as collisional rate coefficients calculated in the 1–20 K range.

*Key words:* astrochemistry – ISM: molecules – molecular processes

### 1. INTRODUCTION

Rotational excitation and de-excitation of molecules are of crucial importance in very low density interstellar media where collisions are not frequent enough to maintain the molecular populations at local thermodynamical equilibrium (LTE). As molecular hydrogen is the dominant colliding partner in most of the molecular regions, inelastic collisions with H<sub>2</sub> play a key role in establishing the observed non-LTE molecular populations. The interpretation of non-LTE spectra thus requires the knowledge of cross sections for collisional excitation induced by H<sub>2</sub>.

Carbon monoxide (CO) is the second most abundant molecule in space after H<sub>2</sub>. In contrast to the latter, which is impossible to observe at low temperatures, CO is the easiest molecule to detect in galaxies, including high-redshift galaxies, and it is systematically used to estimate H<sub>2</sub> densities in molecular clouds. CO transitions, in particular the first two rotational lines  $j_{\text{CO}} = 1 \rightarrow 0$  at 115.271 GHz and  $j_{\text{CO}} = 2 \rightarrow 1$  at 230.538 GHz, are thus among the best tracers of star formation (see, e.g., Omont 2007, and references therein).

In cold and dense molecular regions ( $T \sim 10$  K), H<sub>2</sub> is found mostly in its *para* ground state, ( $j_{\text{H}_2} = 0$ ), due to the *ortho*–*para* conversion (thermalization) of H<sub>2</sub> by reactive collisions with protonated species, in particular H<sup>+</sup> and H<sub>3</sub><sup>+</sup>. In these regions, the *ortho*-to-*para* ratio (OPR) of H<sub>2</sub> is typically 10<sup>−3</sup> (Le Gal et al. 2014). In warmer environments, such as diffuse interstellar clouds or protostellar shocks, the population of *ortho*-H<sub>2</sub>, ( $j_{\text{H}_2} = 1$ , and higher odd levels) increases and the OPR of H<sub>2</sub> can exceed 1 or even approach 3, the high temperature equilibrium value of *normal*-H<sub>2</sub> (see, e.g., Maret et al. 2009). As CO is abundant in both cold and warm regions (see, e.g., Neufeld 2012), collisional excitation of CO by both *para*-( $j_{\text{H}_2} = 0$ ) and *ortho*-H<sub>2</sub> ( $j_{\text{H}_2} = 1$ ) is astrophysically relevant.

The first set of collisional cross sections and rate coefficients for CO + H<sub>2</sub> was obtained by Green & Thaddeus (1976) using a quantum close-coupling treatment of the collision dynamics combined with an approximate (electron gas) potential energy surface (PES). More elaborate PES were determined in the 1980s by using self-consistent field calculations with semiempirical approximations for the dispersion energy (e.g., Schinke et al. 1985). However, the first accurate fully ab initio PES was obtained in the late 1990s by Jankowski & Szalewicz (1998) using the symmetry-adapted perturbation theory (SAPT). More recently, these authors have reported an improved version of their PES where the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)) was adopted (Jankowski & Szalewicz 2005). These two PES will be referred as to  $V_{98}$  and  $V_{04}$ , respectively. The accuracy of the  $V_{04}$  PES was found to be significantly improved. In particular the differences between theoretical and experimental infrared spectral data of the *para*-H<sub>2</sub>–CO complex was reduced from about 1 cm<sup>−1</sup> with  $V_{98}$  to 0.1 cm<sup>−1</sup> with  $V_{04}$  (Jankowski & Szalewicz 2005). Significant differences were also observed in rotational cross sections, especially at low collision energy where the resonance structure is very sensitive to the attractive region of the PES (Wernli et al. 2006). The  $V_{04}$  PES was thus adopted in the recent calculations of Yang et al. (2010), who have provided the most accurate set of inelastic rate coefficients. We note that this set was extrapolated to include states with  $j_{\text{CO}} > 40$  by Neufeld (2012).

Recently, Chefdeville et al. (2012) have reported a crossed beam experiment on CO + *para*-H<sub>2</sub> where the relative integral cross section (ICS) for the transition  $j_{\text{CO}} = 0 \rightarrow 1$  was measured at low energy in the threshold region. The resonance structure was resolved experimentally for the first time in an inelastic collision. A qualitative agreement with theoretical calculations based on the  $V_{04}$  PES was also obtained. However, Chefdeville et al. (2012) found it necessary to scale the  $V_{04}$  PES by a factor of 1.05 in order to reproduce the resonance positions:

it was consistent with the scaling factor of 1.042 suggested by Jankowski & Szalewicz (2005) to improve the agreement between theoretical and experimental second virial coefficients at low temperature. Later, an experimental bias was discovered in the ICS treatment of Chefdeville et al. (2012) and corrected data have been published very recently by Naulin & Costes (2014). This correction was found to significantly improve the agreement with the theoretical ICS based on the scaled  $V_{04}$  PES.

As discussed by Jankowski & Szalewicz (2005), the precision of the  $V_{04}$  PES was insufficient to assign the *ortho*-H<sub>2</sub>-CO spectrum and further increase in accuracy of the PES was necessary. To decrease the uncertainty of the theoretical predictions below 0.1 cm<sup>-1</sup>, Jankowski et al. (2012) then computed a new PES with inclusion of complete triple and noniterative quadruple excitations [CCSDT(Q)]. They also increased the size of basis sets as well as the dimensionality of the grid used in the ab initio calculations to the full six dimensions, whereas  $V_{98}$  was based on the four-dimensional grid and  $V_{04}$  on the five-dimensional one. The ab initio energies obtained for the six-dimensional grid have been averaged over the ground vibrational states of H<sub>2</sub> and CO and the final fit to the averaged energies is referred to as  $V_{12}$ . Note that a surface averaged over the first excited state of CO was also developed, but was not used in the present work. For most lines of the *ortho*-H<sub>2</sub>-CO complex, agreement to within 0.01 cm<sup>-1</sup> between experiment and theory was achieved. In their recent article, Jankowski et al. (2013) have compared in detail the  $V_{12}$  and  $V_{04}$  PES. They have shown in particular that the two PES differ by only  $\sim 1$  cm<sup>-1</sup> in the well depth but that such subtle difference increases the accuracy on spectral data by about an order of magnitude. On the other hand, very small changes were observed for the dissociation energy and virial coefficients, which led Jankowski et al. (2013) to conclude that a scaling of the  $V_{04}$  PES cannot be justified.

In this Letter, we report new crossed-beam measurements and scattering calculations for the rotational excitation of CO( $j_{\text{CO}} = 0 \rightarrow 1$ ) by *normal*-H<sub>2</sub>, i.e., a ratio of 0.25/0.75 of *para*- and *ortho*-H<sub>2</sub>, respectively, and the rotational excitation of CO( $j_{\text{CO}} = 2$ ) by *para*-H<sub>2</sub>. Since the experiment is sensitive only to the final population of  $j_{\text{CO}} = 2$  state, one has to include excitations from  $j_{\text{CO}} = 0$  and  $j_{\text{CO}} = 1$ . New scattering calculations were also performed for the rotational excitation of CO( $j_{\text{CO}} = 0 \rightarrow 1$ ) by *para*-H<sub>2</sub> with the  $V_{12}$  PES and compared to the older experimental results. We show that the measured resonance structures are now in good quantitative agreement with the calculations, suggesting that theory and experiment have converged for this benchmark system.

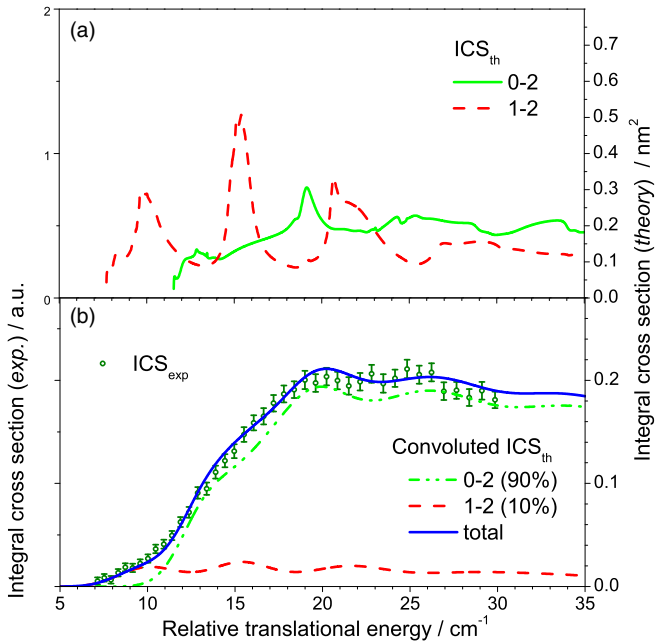
## 2. EXPERIMENT

The ICS for collisional excitation of CO by *para*-H<sub>2</sub> has already been observed for the  $j_{\text{CO}} = 0 \rightarrow 1$  transition (Chefdeville et al. 2012). Using the same apparatus as the one described in that study, we measured the ICS corresponding to the  $j_{\text{CO}} = 0 \rightarrow 2$  and  $j_{\text{CO}} = 1 \rightarrow 2$  transitions by probing the collision-induced population enhancement of the  $j_{\text{CO}} = 2$  level as a function of the collision energy using the (2+1) ( $E^1\Pi, v = 0 \leftarrow X^1\Sigma_g^+, v = 0$ ) resonance-enhanced multiphoton ionization (REMPI)  $P(2)$  transition at 46461.2 cm<sup>-1</sup> (215.23 nm) (Hines et al. 1990). The *para*-H<sub>2</sub> beam purity was checked by recording ( $C^1\Pi_u, v = 2 \leftarrow X^1\Sigma_g^+, v = 0$ ) $R(0)$  and  $R(1)$  (3+1) REMPI transitions near 34530 cm<sup>-1</sup> (289.6 nm), respectively (Pratt et al. 1984), from which a population ratio

$>95\%$  for  $j_{\text{H}_2} = 0$  was inferred. The ICSs were also measured for the  $j_{\text{CO}} = 0 \rightarrow 1$  collisional excitation of CO by *normal*-H<sub>2</sub>, i.e., with the high temperature OPR limit value of 3. The initial residual population in  $j_{\text{CO}} = 1$  (or  $j_{\text{CO}} = 2$ ) level, estimated to be ca. 1% (or  $<0.01\%$ ) relative to  $j_{\text{CO}} = 0$  (Chefdeville et al. 2012), was offset by shot-to-shot background subtraction when triggering the probe laser and the CO beam at 10 Hz with the H<sub>2</sub> beam at 5 Hz. The ICSs were recovered from the measured intensities using the procedure introduced for the O<sub>2</sub> + H<sub>2</sub> inelastic collisions described in the Supplementary Materials of Chefdeville et al. (2013). Briefly, it was shown that for nearly thermoneutral processes, the detected species propagate almost in phase with the reactants, resulting in an interaction time increasing at decreasing crossing angles. This effect is more pronounced when using beams of matched velocities and for heavy-light collisions when detecting the heavy partner, which is the case here. This treatment, described in Naulin & Costes (2014), was also applied to the experimental data obtained previously for the  $j_{\text{CO}} = 0 \rightarrow 1$  transition (Chefdeville et al. 2012) in order to allow comparison with the new scattering calculations performed with the  $V_{12}$  PES. To allow for comparison with theory, each experimental ICS is rescaled to the same area as the theoretical one within their common energy range.

## 3. THEORY

The close-coupling calculations presented in our previous work (Chefdeville et al. 2012) were complemented using again our code DIDIMAT which was first developed to study the H<sub>2</sub>-HF collisions (Guillon et al. 2008) and used henceforth to study other diatom-diatom collisions such as H<sub>2</sub>-CS (Denis-Alpizar et al. 2013). The close-coupling equations were propagated in the space-fixed frame using a log-derivative propagator and the rigid rotor approximation, which assumes that the dependence of the interaction energy on the intramonomer coordinates can be neglected. This long standing approximation stems from the fact that the monomer vibrational frequencies are much higher than the intermolecular ones. The optimal choice of the monomer geometries in calculations of intermolecular interaction energies within this approximation was discussed by several authors (Jeziorska et al. 2000; Le Roy & Hutson 1987). The main conclusion of these studies was that the best choice corresponds to the vibrationally averaged potential, which was adopted here. The values of the rotational constants of CO and H<sub>2</sub> were fixed to  $B_0(\text{CO}) = 1.9225$  cm<sup>-1</sup> and  $B_0(\text{H}_2) = 59.322$  cm<sup>-1</sup>. The highest rotational level of CO used in all calculations was  $j_{\text{CO}} = 15$  while two rotational levels of H<sub>2</sub> were included for both the *para* ( $j_{\text{H}_2} = 0, 2$ ) and *ortho* ( $j_{\text{H}_2} = 1, 3$ ) species of H<sub>2</sub>, which was sufficient to reach convergence, as the H<sub>2</sub> rotational energy spacing is large. This was further confirmed by a test calculation with inclusion of  $j_{\text{H}_2} = 4$  for *para*-H<sub>2</sub> which led to quite negligible changes. The propagation was carried out to a maximum distance of 100  $a_0$  for the lowest energy and convergence was checked as a function of the propagator step size. At each energy, a 10<sup>-6</sup> relative convergence of the inelastic cross sections as a function of the total angular momentum  $J$  was ensured. Calculations were performed using both the  $V_{04}$  and  $V_{12}$  PESs. These two PES were fitted using a spherical harmonics expansion including all anisotropies up to  $l_1 = 10$  for CO and  $l_2 = 6$  for H<sub>2</sub> (where the integer indices  $l_1$  and  $l_2$  refer to the tensor ranks of the angular dependence of the CO and H<sub>2</sub> orientation, respectively), resulting in 142 angular terms (Wernli et al. 2006).

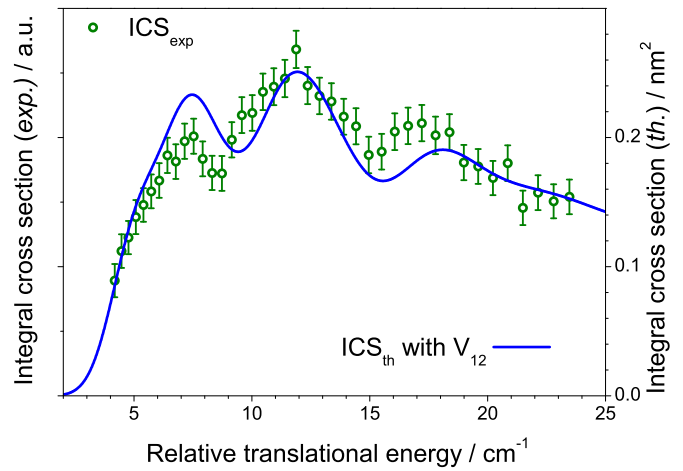


**Figure 1.** Collisional energy dependence of the integral cross sections for CO excitation ( $j_{\text{CO}} = 0, 1 \rightarrow 2$ ) by *para*-H<sub>2</sub>. (a) Theoretical ICSs calculated with  $V_{12}$  PES (Jankowski et al. 2012) for both possible transitions  $0 \rightarrow 2$  and  $1 \rightarrow 2$ , (b) comparison of theoretical ICSs convoluted with the experimental collision energy spread (solid blue line), with a 10% relative contribution of collisions with CO( $j_{\text{CO}} = 1$ ) with experimental data (open circles) in arbitrary units. The measurements were performed when crossing a beam of neat *para*-H<sub>2</sub> from a pulsed nozzle at ca. 45 K propagating at velocity  $v_1 = 943 \text{ ms}^{-1}$  with a beam of 1% CO in He from another pulsed nozzle at ca. 85 K propagating at  $v_2 = 941 \text{ ms}^{-1}$ ; crossing angle  $\chi$  was varied from 17.5 to 37.5, resulting in a collision energy  $E_T = (1/2)\mu(v_1^2 + v_2^2 - 2v_1v_2 \cos\chi)$  where  $\mu$  stands for the reduced mass of the collision partners.

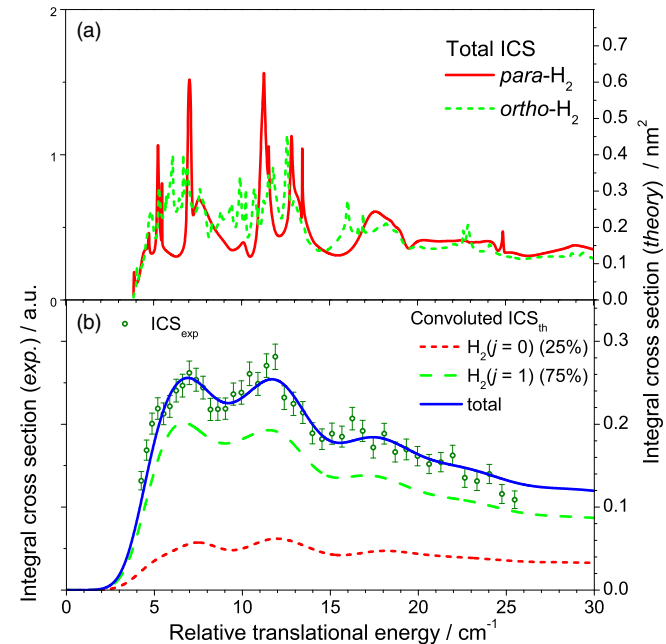
#### 4. RESULTS

The results obtained for CO ( $j_{\text{CO}} = 0, 1 \rightarrow 2$ ) excitation by collision with H<sub>2</sub> are displayed in Figure 1: the theoretical ICSS, calculated with the  $V_{12}$  PES of Jankowski et al. (2012) are given in panel (a); experimental data are displayed in panel (b), along with the theoretical ICSs convoluted with experimental energy spread to allow for comparison. The theoretical data displayed in Figure 1(b) are the sum of the contributions of excitation from the  $j_{\text{CO}} = 0$  and 1 states. The populations of rotational level with  $j_{\text{CO}} \geq 2$  are below than our detection limit: therefore the de-excitation contributions from these levels need not be taken into account. The  $1 \rightarrow 2$  ICS was included as a 10% contribution to the total ICS based on average population of the  $j_{\text{CO}} = 1$  state in the experiment. Note that this contribution does not correspond to the  $j_{\text{CO}} = 1$  population determined when probing the central part of the beam (ca. 1%, corresponding to a rotational temperature close to 1 K); in this collision experiment, half the CO beam (from its rising edge to the middle of the pulse) contributes to the signal; since  $j_{\text{CO}} = 1$  populations are higher on the edges (up to  $\sim 15\%$  at the maximum of the signal for  $j_{\text{CO}} = 1$ ), the overall contribution due to collisions of CO( $j_{\text{CO}} = 1$ ) with H<sub>2</sub> also is higher (10%, corresponding to an average temperature within the whole beam of about 1.6 K). Such a contribution describes well the behavior of the total ICS below the  $0 \rightarrow 2$  threshold.

The experimental data on the  $0 \rightarrow 1$  transition, as published by Chefdeville et al. (2012), were not corrected for the variation of the mean interaction time with the beam crossing angle. Furthermore, the calculations presented in this Letter were



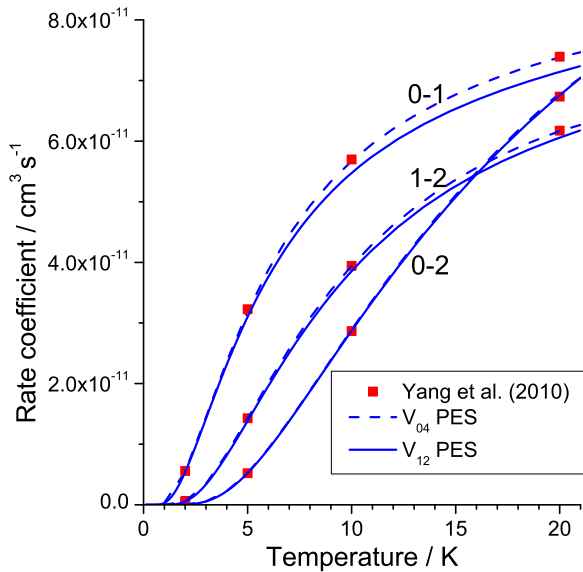
**Figure 2.** Integral cross-sections for the CO rotational transition  $0 \rightarrow 1$  induced by *para*-H<sub>2</sub> as function of collision energy. The corrected experimental data (Naulin & Costes 2014; same conditions as Figure 1) is compared to the new theoretical ICS calculated with the  $V_{12}$  PES and convoluted with the experimental energy spread.



**Figure 3.** Collisional energy dependence of the integral cross sections for CO excitation ( $j_{\text{CO}} = 0 \rightarrow 1$ ) by *normal*-H<sub>2</sub>. (a) Theoretical ICSs calculated with  $V_{12}$  PES (Jankowski et al. 2012) for *para*- and *ortho*-H<sub>2</sub>; (b) theoretical ICSs convoluted with the experimental collision energy spread (solid blue line), with a 25% relative population of *para*-H<sub>2</sub> ( $j_{\text{H}_2} = 0$ ) and 75% of *ortho*-H<sub>2</sub> ( $j_{\text{H}_2} = 1$ ); experimental data (open circles) in arbitrary units (for more details, see the caption of Figure 1).

performed using the former  $V_{04}$  PES (Jankowski & Szalewicz 2005), rescaled by a factor of 1.05 to obtain a fair agreement (i.e., reproducing the position of the peaks). These former experimental data were corrected, similarly as we did for the  $0, 1 \rightarrow 2$  transitions. The comparison of uncorrected and corrected experimental ICSs, with calculations using the scaled  $V_{04}$  PES can be found in Figure 9 of Naulin & Costes (2014). These experimental results, along with new theoretical calculations performed on the  $V_{12}$  PES, are displayed in Figure 2.

To allow comparison with *ortho*-H<sub>2</sub>, experimental measurements on the  $0 \rightarrow 1$  rotational excitation of CO by *normal*-H<sub>2</sub> were performed (see Figure 3): the theoretical ICSs for *para*- and *ortho*-H<sub>2</sub>, calculated with the  $V_{12}$  PES of Jankowski et al.



**Figure 4.** Rate coefficients for the three CO rotational transitions  $j_{\text{CO}} = 0 \rightarrow 1$ ,  $j_{\text{CO}} = 0 \rightarrow 2$  and  $j_{\text{CO}} = 1 \rightarrow 2$  induced by *para*-H<sub>2</sub> as a function of temperature. The set of theoretical data of Yang et al. (2010) is compared to the present calculations performed on the  $V_{04}$  (dashed lines) and  $V_{12}$  PES (solid lines).

(2012) are given in panel (a); experimental data of CO + *normal*-H<sub>2</sub> are displayed in panel (b), along with the theoretical ICSs convoluted with experimental energy spread and the *para*- and *ortho*-H<sub>2</sub> contributions weighted to their relative populations in *normal*-H<sub>2</sub>, i.e., 1/4 and 3/4, respectively.

A good accord is found between all the present experimental data and theoretical calculations. The agreement in Figures 1 and 3 is excellent and almost within error bars. The data obtained with *para*-H<sub>2</sub> for CO( $j_{\text{CO}} = 0 \rightarrow 1$ ) (see Figure 2), however, exhibit some differences for the location of maxima and minima which are the resonance signatures. We note that these slight differences cannot be significantly reduced when using a rescaled PES for the calculations. Furthermore, for the other data (Figures 1 and 3), the experimental behavior is better rendered without any scaling factor, especially at low energies, where the experimental spread is the smallest. From the overall good agreement between theory and experiment, we conclude that the  $V_{12}$  PES can be confidently used to derive thermal collisional rate coefficients, as illustrated below.

The rotational rate coefficients were computed by averaging the above cross sections over Maxwell–Boltzmann velocity distributions. In Figure 4 the rates obtained using the  $V_{04}$  and  $V_{12}$  PES are reported, as well as the results of Yang et al. (2010), for the three transitions  $j_{\text{CO}} = 0 \rightarrow 1$ ,  $0 \rightarrow 2$  and  $1 \rightarrow 2$ . As expected, our calculations based on the  $V_{04}$  PES are in perfect agreement with those of Yang et al. (2010) performed with the same PES. The new rates computed with the  $V_{12}$  PES are very similar, with differences not exceeding 5%, in this temperature range.

## 5. CONCLUSION

In summary, we have performed new experiments, with a crossed molecular beam apparatus, on the rotational excitation of CO by collisions with *para*- and *normal*-H<sub>2</sub>. The ICS’s dependences on collision energy between ca. 4 and 30 cm<sup>-1</sup> were recorded for the CO ( $j_{\text{CO}} = 0, 1 \rightarrow 2$ ) excitation by *para*-H<sub>2</sub> and CO ( $j_{\text{CO}} = 0 \rightarrow 1$ ) excitation by *normal*-H<sub>2</sub> (0.25:0.75 mixture of *para*-H<sub>2</sub> and *ortho*-H<sub>2</sub>). New close-coupling calculations on the  $V_{12}$  PES of Jankowski et al. (2012) yield ICSs which, when convoluted with experimental energy resolution, compare well with all the experimental data, including the previous ones on CO ( $j_{\text{CO}} = 0 \rightarrow 1$ ) excitation by *para*-H<sub>2</sub>. The generally good agreement between experimental and theoretical results reinforces the confidence in the observables derived from the  $V_{12}$  PES, since the scattering calculations are very sensitive to the accuracy of the potential, especially in the entrance valley. We note, however, that although resonances contribute significantly to the thermal rate coefficients in the 1–20 K range, the resonance features observed in the excitation functions are essentially blurred out by thermal averaging. Consequently, the differences (in the well depth and anisotropy) between the  $V_{04}$  and  $V_{12}$  PES do not result in a significant difference in the thermal rates derived from these potentials. The extensive set of collisional data computed by Yang et al. (2010) with the  $V_{04}$  PES can therefore be reliably used.

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