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Pressure broadening of water and carbon monoxide transitions by molecular hydrogen at high temperatures

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ABSTRACT

Water and carbon monoxide are two major compounds in the predominantly H_2 atmospheres of stars, brown dwarfs and extrasolar planets. Recent radiative transfer models suggest that there is an urgent need for data on the pressure broadening of molecular transitions by H_2 at high temperatures. We present a set of theoretical H_2 pressure broadening parameters for 228 H_2O transitions in the range of 10–20,000 GHz and 30 CO transitions in the 115–3500 GHz region. These parameters are appropriate for temperatures between 200 and 3000 K. The random phase approximation is employed to derive the broadening parameters from recent state-of-the-art inelastic collisional rate coefficients. This approximation is compared both to full close-coupling calculations and to available experimental data. It is shown to be valid at temperatures above 200 K, as expected from theoretical considerations, with an accuracy of about 25%.

1. Introduction

A knowledge of spectral line shapes as a function of pressure and temperature is crucial to both (1) interpreting remote sensing spectroscopy measurements of the atmospheres of stars and planets at microwave and infrared frequencies and (2) for models of radiative transport in these atmospheres. There is growing evidence that the correct treatment of pressure broadening by molecular hydrogen of both water [1] and carbon monoxide [2] is important for the correct representation of the atmospheres of "hot Jupiter" extrasolar planets and brown dwarfs. For these objects pressure broadening parameters are required at elevated temperatures: typically in the range of 500–3000 K.

For non-overlapping spectral transitions, the line shape is well represented by a Lorentzian with a width (and shift) proportional to pressure convoluted with a Gaussian to represent thermal broadening effects. The resulting Voigt profiles are extensively used to model line shapes in Earth's and other atmospheres where methods for deriving pressure broadening parameters from both theory and experiment are well developed [3]. Measurements of H_2 broadening of CO [4–6] and H_2O [7–9] and closely related theoretical calculations [9–11] provide a basis of comparison for the present work. However, there are few measurements of pressure broadening parameters at elevated temperatures, where the number of lines which are important increases significantly [12]. Similarly, while there has been some work on extrapolating pressure broadening parameters to higher rotational states [13–15], standard theoretical procedures are not well adapted to work at higher temperatures. Fully close-coupling methods become increasingly expensive with rising temperature and so far have only proved practical

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for temperatures below 600 K for H_2–CO [4] and 250 K for H_2–H_2O [11,9]. Conversely semi-empirical methods, which rely on comparisons with experimental data, cannot easily be extended to temperature regimes for which no such data is available.

In this work we use the random phase approximation (RPA) to considerably simplify the calculation of line broadening parameters. We demonstrate that this approximation becomes reliable with increasing temperatures. We present line broadening coefficients as a function of temperature for the H_2–CO and H_2–H_2O systems. This data can be used in conjunction with the extensive transition frequency and transition intensity data provided by the ExoMol project [16] which aims to provide comprehensive data for modelling radiative transport properties and spectra of extrasolar planets and cool stars. This paper is organized as follows: in Section 2, we present the RPA and the method we have employed to derive the broadening parameters from the available inelastic collisional rate coefficients. Comparisons between the RPA, close-coupling calculations and broadening measurements are presented in Section 3 for both water and carbon monoxide. Conclusions are drawn in Section 4.

2. Theory

Within the impact approximation, which assumes that the collision time is much shorter than the time interval between collisions, the pressure broadening cross section $\sigma^{\rm PB}(f\leftarrow i;E_{\rm coll})$ of an isolated line $f\leftarrow i$ can be expressed as a function of *elastic* scattering *S*-matrix elements within the quantum close-coupling (CC) approach [17]. Explicit formulae have been derived several times and can be found in e.g. [11]. Alternatively, the pressure broadening (PB) cross section can be related to the total inelastic state-to-state cross sections and to a pure elastic term *via* the optical theorem [17]:

$$\sigma^{\rm PB}(f\leftarrow i;E_{\rm coll})=\frac{1}{2}\left[\sum_{f'\neq i}\sigma^{\rm in}(f'\leftarrow i;E_{\rm coll})+\sum_{f'\neq f}\sigma^{\rm in}(f'\leftarrow f;E_{\rm coll})\right]+\int\left|f_i(\Omega;E_{\rm coll})-f_f(\Omega;E_{\rm coll})\right|^2\,{\rm d}\Omega, \quad (1)$$

where $\sigma^{\rm in}(f'\leftarrow i;E_{\rm coll})$ and $\sigma^{\rm in}(f'\leftarrow f;E_{\rm coll})$ are ordinary inelastic state-to-state cross-sections, $f_i(\Omega;E_{\rm coll})$ and $f_f(\Omega;E_{\rm coll})$ are the differential elastic scattering amplitudes and $d\Omega$ is the element of solid angle. The elastic contribution, which includes both reorientation and dephasing effects, is strictly zero only for isotropic Raman *Q* lines. It is also ignored within the RPA [18] but it cannot be neglected *a priori*. This was shown remarkably by the measurements of Ball and De Lucia [19] where elastic collisions were found to dominate the broadening of H_2S by He below 40 K.

Recently, the RPA was also found to fail in the case of the broadening of H_2O by H_2 below about 200 K [11]. The substantial role of elastic collisions at low temperature can be attributed at least partly to the formation of quasi-bound states of the complex. Indeed, significant resonances in the PB cross sections are present in the rotationally elastic cross sections but absent in the rotationally inelastic cross sections, as observed in CO–He [19] and more recently in HCO^+–He [20] and H_2O–H_2 [9]. These resonances, as those observed in the inelastic cross sections, occur when the collision energy is transferred to rotation and the colliders are temporarily trapped in the potential well. These effects are thus expected to vanish when the collision (or rotational) energy exceeds the depth of the potential well, which lies in the range of 10–300 $\rm cm^{-1}$ for typical van der Waals systems. Above room temperature, the RPA is therefore expected to hold. DePristo and Rabitz [18] have also shown that the accuracy of the RPA should increase with increasing rotational quantum number *j*. The good agreement between the RPA and exact PB calculations at high collision energies and for high rotational levels was indeed observed for various systems, e.g. HCl–Ar [21] and more recently CO_2–Ar [22].

In this work, we are interested in the broadening of water and carbon monoxide by hydrogen molecules at temperatures above 300 K. It should be noted that comparisons between theoretical and experimental pressure broadening cross sections were previously published for these systems but with an emphasis on the low temperature regime [11,9,4]. These previous works are discussed in Section 3. Here we have employed the RPA, i.e. the integral over the solid angle in Eq. (1) was omitted, assuming that at these temperature linewidths may be considered as a simple sum of inelastic cross sections. This is a very useful approximation because extensive sets of rotationally inelastic rate coefficients (i.e. cross sections, see below) have been made available recently for water [23] and carbon monoxide [24]. These rate coefficients are indeed crucial to interpret the H_2O and CO (sub)millimetre spectra in astronomical environments where the rotational levels are not in local thermodynamic equilibrium (LTE), see e.g. [25]. These inelastic rate coefficients have been computed at the quantum CC level using state-of-the-art potential energy surfaces (PES). Both the CO–H_2 [26] and H_2O–H_2 [27] PES were indeed determined by combining the coupled-cluster method with single, double, and non-iterative triple excitations [CCSD(T)] with basis sets close to the basis set limit. The accuracy of the CO–H_2 and H_2O–H_2 PES (about 1 $\rm cm^{-1}$ in the potential well) was checked against various measurements, in particular state-to-state cross sections [28,29] and the ro-vibrational spectra of the van der Waals complexes [26,30]. The theoretical results were found to agree very well with the experimental data, providing support for the reliability of the calculated inelastic rate coefficients.

The inelastic state-to-state rate coefficients computed by Yang et al. [24] for CO–H_2 and by Daniel et al. [23] for H_2O–H_2 depend on the angular momentum j_2 of H_2 which, in turn, depends on the nuclear spin of H_2: $I=0$ for para-H_2 and $I=1$ for ortho-H_2. Indeed, in the ground electronic state, the rotational levels of para-H_2 have even values of the angular momentum j_2 (0, 2, …), while the levels of ortho-H_2 have odd j_2 values (1, 3, …). Since the ortho-to-para ratio of H_2 in thermal equilibrium is equal to 3 above about 200 K ('normal' H_2), the PB cross section at temperature $T>200$ K of a rotational line $f\leftarrow i$

is computed as a sum of two contributions

$$\sigma^{\mathrm{PB}}(f \leftarrow i;T) = \tfrac{1}{4}\,\sigma^{\mathrm{PB}}_{\mathrm{pH_2}}(f \leftarrow i,T) + \tfrac{3}{4}\sigma^{\mathrm{PB}}_{\mathrm{oH_2}}(f \leftarrow i;T), \qquad (2)$$

where, within RPA, the PB cross sections $\sigma_{\mathrm{pH_2}}(f \leftarrow i;T)$ and $\sigma_{\mathrm{oH_2}}(f \leftarrow i;T)$ are given by the sum of inelastic cross sections, e.g. for para-H_2:

$$\sigma^{\mathrm{PB}}_{\mathrm{pH_2}}(f \leftarrow i;T) = \frac{1}{2}\left[\sum_{f' \neq i}\sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f' \leftarrow i;T) + \sum_{f' \neq f}\sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f' \leftarrow f;T)\right]. \qquad (3)$$

It should be noted that the differences between the inelastic cross sections corresponding to para-H_2 and ortho-H_2 are substantial at low temperatures for H_2O [11,23] while they are moderate for CO [4,24].

In practice, the Maxwell–Boltzmann thermal average inelastic cross sections, e.g. for para-H_2

$$\sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;T) = \frac{1}{(\mathrm{k}_B\mathrm{T})^2}\int \sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;E_{\mathrm{coll}})E_{\mathrm{coll}}\exp(-E_{\mathrm{coll}}/k_BT)\mathrm{d}E_{\mathrm{coll}} \qquad (4)$$

were computed as

$$\sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;T) = k^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;T)/\overline{v}, \qquad (5)$$

where $k^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;T)$ is a "thermalized" inelastic rate coefficient and $\overline{v}$ is the mean relative velocity

$$\overline{v} = \sqrt{\frac{8k_BT}{\pi\mu}}, \qquad (6)$$

with μ being the reduced mass of the colliding pairs. We note that these thermalized rate coefficients do not depend on the angular momentum j_2 because they have been summed and averaged over the H_2 rotational populations

$$k^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i;T) = \sum_{j_2,j_2'\ \mathrm{even}} \rho(j_2)k^{\mathrm{in}}_{\mathrm{pH_2}}(f,j_2' \leftarrow i,j_2;T) \qquad (7)$$

and

$$k^{\mathrm{in}}_{\mathrm{oH_2}}(f \leftarrow i;T) = \sum_{j_2,j_2'\ \mathrm{odd}} \rho(j_2)k^{\mathrm{in}}_{\mathrm{oH_2}}(f,j_2' \leftarrow i,j_2;T), \qquad (8)$$

where $\rho(j_2)$ are the (normalized) Maxwell–Boltzmann populations of each H_2 spin species and $k^{\mathrm{in}}_{\mathrm{pH_2}}(f,j_2' \leftarrow i,j_2;T)$ and $k^{\mathrm{in}}_{\mathrm{oH_2}}(f,j_2' \leftarrow i,j_2;T)$ are the state-to-state inelastic rate coefficients, as computed by Yang et al. [24] and by Daniel et al. [23]. The thermalized inelastic rate coefficients, Eqs. (7) and (8), are available online at the LAMDA[1] and BASECOL[2] web sites. The data cover the temperature ranges 5–1500 K and 2–3000 K and include the lowest 90 levels of H_2O (45 para-H_2O and 45 ortho-H_2O) and 41 levels of CO, respectively. We have found that expansion of the basis to at least 10 energy levels beyond the desired quantum number range is necessary for convergence of the sums in Eq. (3) to better than 10%. In practice, we have therefore restricted the broadening data to the lowest 71 ($J < 10$) and 31 ($J < 31$) levels of H_2O and CO, respectively. It should be noted that in the case of CO, para-H_2 and ortho-H_2 were restricted to their lowest $j_2 = 0$ and $j_2 = 1$ levels in the calculations of Yang et al. [24]. As there is only a small difference between the inelastic cross sections for H_2 in $j_2 = 1$ and in $j_2 > 1$, we weight the $j_2 = 0$ cross sections with the thermal distribution of $j_2 = 0$ and the $j_2 = 1$ cross sections with the thermal distribution of all levels with $j_2 \geq 1$.

Finally, the cross sections were converted to the normalized halfwidths at half maximum (HWHM), i.e. the broadening parameters $\gamma(f \leftarrow i;T)$, using the relation

$$\gamma(f \leftarrow i;T) = \frac{\overline{v}\sigma^{\mathrm{PB}}(f \leftarrow i;T)}{2\pi k_bT} = 2.236\frac{\sigma^{\mathrm{PB}}(f \leftarrow i;T)}{\sqrt{\mu T}}, \qquad (9)$$

where the cross section is in Å^2, the temperature is in K, μ is the reduced mass in amu and $\gamma(f \leftarrow i;T)$ is in MHz/Torr. The reduced masses were taken as 1.812774 and 1.880287 for H_2O–H_2 and CO–H_2, respectively.

3. Results

3.1. Water

In Fig. 1 the PB parameters for water transitions in the range of 183–1113 GHz are plotted as functions of temperature in the range of 10–1500 K. Transitions are displayed in the increasing order of frequency. In the two upper panels, corresponding to the transitions at 183 and 380 GHz, the RPA results are compared to the measurements of Dutta et al. [7] which cover the range of 103–520 K. The agreement between the RPA and experimental data is found to improve with temperature, as expected: the relative differences decrease from about 35% at 100 K to 10–15% at the highest measured temperatures. This is fully consistent with the theoretical considerations explained above and suggests that the elastic contribution in the H_2 broadening of H_2O lines becomes significant only below room temperature. In the three other panels, the RPA results are compared to the recent measurements and CC calculations of Drouin and Wiesenfeld [9]. We can first observe the very good agreement found by these authors between the CC approach, which rigorously includes the elastic contribution, and the measurements, especially for the 556 GHz transition where the agreement is within error bars. We note that the small deviation above 50 K between the CC results and the experimental 1113 GHz data only reflects a poor convergence of the theoretical Maxwell–Boltzmann average. Full details can be found in Drouin and Wiesenfeld [9]. As the experimental data was restricted to temperatures below 224 K, no comparison above room temperature is possible for these transitions. However, the RPA results and the experimental points are found to agree within about 30% at the highest reported temperatures (between 145 and 224 K). Again, elastic collisions appear to be significant or even dominant at $T < 200$ K: the RPA indeed underestimates the broadening parameters by up to a factor of 4 at 20 K. We thus observe that the RPA results above 200 K and the CC calculations below 100 K are compatible, as expected. Indeed, when the same PES is employed, the CC calculations must converge towards the (high temperature) RPA values.

Three additional transitions were measured *via* the same techniques described in Drouin and Wiesenfeld [9]. These transitions have the quantum numbers of $3_{0,3}$–$3_{1,2}$, $2_{2,1}$–$3_{1,2}$ and $3_{1,2}$–$3_{2,1}$ and lower state energies of 136.76,

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[1] http://home.strw.leidenuniv.nl/~moldata/

[2] http://basecol.obspm.fr/

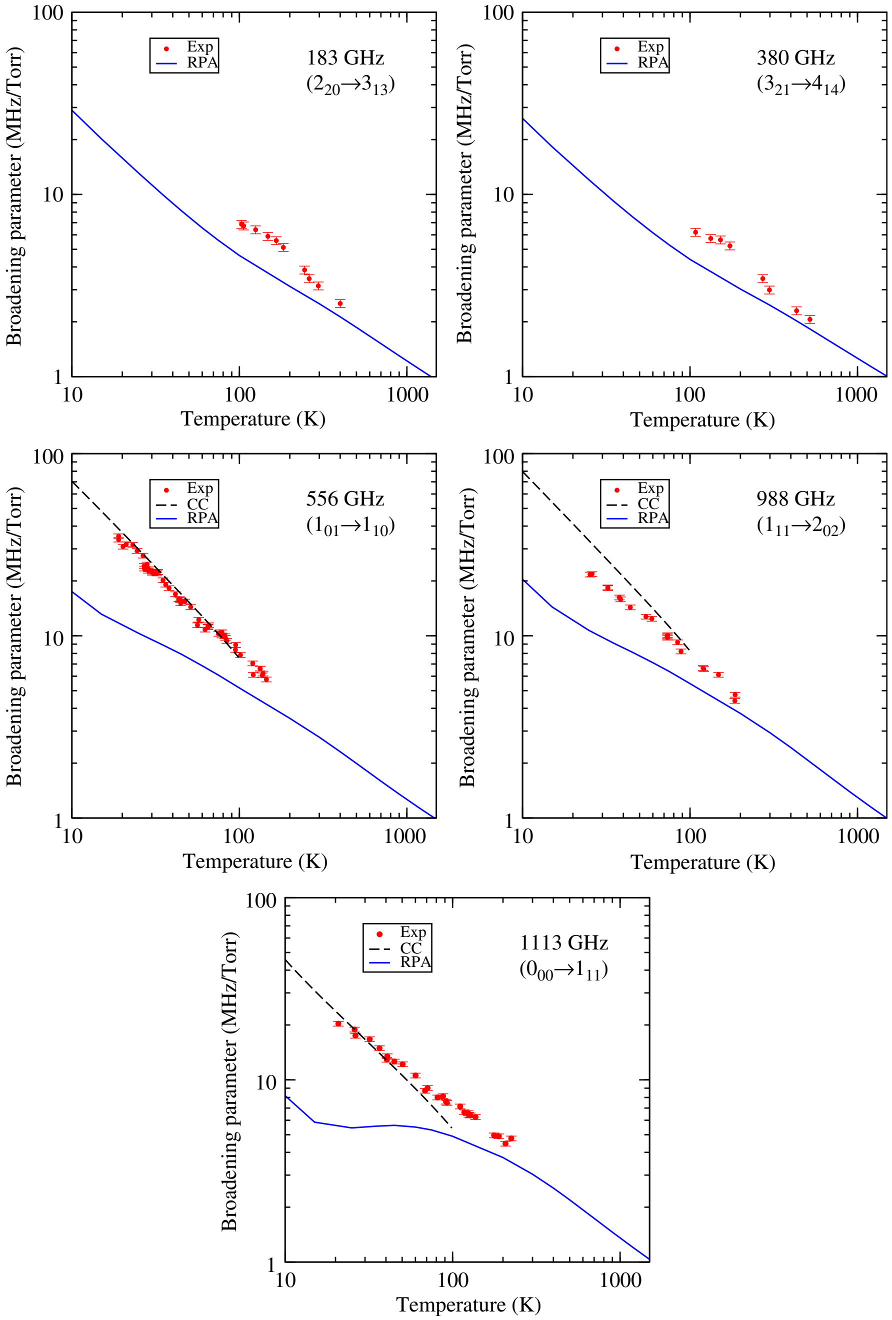

Fig. 1. Broadening parameter (in MHz/Torr) as a function of temperature for five transitions of H_2O in collision with *n* H_2. The experimental data (red circles with error bars) at 183 and 380 GHz are taken from Dutta et al. (1993). CC calculations (dashed black line) and experimental data at 556, 988 and 1113 GHz are taken from Drouin and Wiesenfeld (2012). The present RPA results are given by the solid blue lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

134.90 and 173.37 cm^{-1}, respectively. Due to the thermal excitation required for these measurements the lowest measured temperatures were limited to 33, 68 and 68 K. Furthermore, detailed scattering calculations of states with this excitation level were beyond the scope of the comparative work presented in Drouin and Wiesenfeld [9]. Therefore, we report the experimental values here to complete the published experimental data set and to provide further comparison data points for the RPA results. The data points shown in Fig. 2 are those recorded in 'normal' hydrogen gas, where the ortho/para ratio is held at its room temperature value of three. This data predominately represents three parts $j_2=1$ hydrogen to one part $j_2=0$ hydrogen, although the $j_2=2$ component is relevant at the highest temperatures. The experimental work also included measurements of specially prepared 'para' hydrogen, which includes (at these temperatures) a statistical mixture of $j_2=0$ and $j_2=2$ hydrogen gas. All of

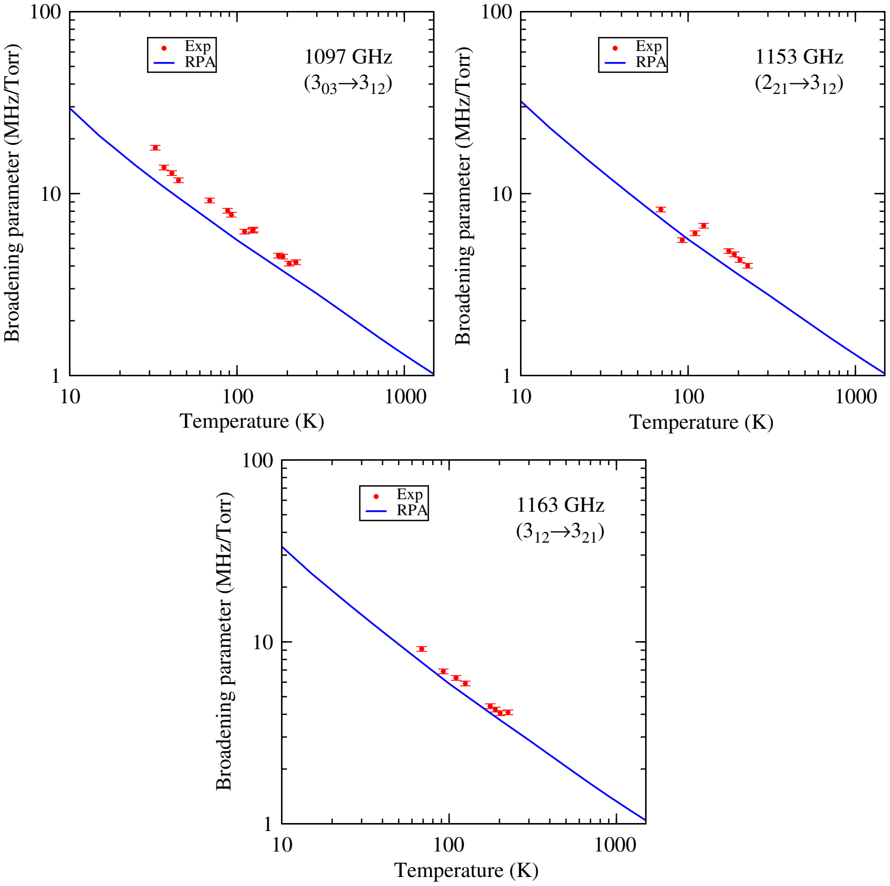

Fig. 2. Broadening parameter (in MHz/Torr) as a function of temperature for three transitions of ortho-H_2O in collision with *n* H_2. The experimental data (red circles with error bars) is from the present work. The RPA results are given by the solid blue lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this data are provided in Supplementary Tables S1–S3 [35,36].

For these three transitions, the agreement between the RPA and the measurements is within 20% and does not significantly change with increasing temperature. This probably reflects the fact that the transitions displayed correspond to relatively high lying levels ($j \geq 2$) for which the RPA even applies at low temperature, as discussed in Section 2.

In summary, the RPA combined with state-of-the-art inelastic rate coefficients is found to reproduce the available H_2O–H_2 broadening experimental data within 20–30% above about 200 K and a similar agreement is observed at even lower temperature for high lying transitions. The above comparisons also confirm once more the high accuracy of the H_2O–H_2 PES [27] employed. The RPA was in practice employed with the full set of thermalized inelastic rate coefficients computed by Daniel et al. [23] (see above), providing broadening parameters for 228 water transitions in the frequency range of 10–20,000 GHz, corresponding to energy levels lower than 1100 cm^{-1}, and for temperatures between 200 and 1500 K.

For modelling purpose, we have fitted our data using the standard relation

$$\gamma(T) = \gamma_0 (T_0/T)^{\beta}, \qquad (10)$$

where γ_0 is the broadening parameter at the reference temperature T_0, taken here as 296 K, and β is a constant. Eq. (10) was found to reproduce our data within 5% or better. The two fitting parameters (γ_0 and β) are provided in Supplementary Tables which are also available on the ExoMol web site.[3] We emphasize that these fits are only valid in the temperature range of $200 \leq T \leq 1500$ K. It can be noticed from Tables S4 and S5 that β lies in the range of 0.3–0.8, i.e. it is close to the value of 0.5 predicted by hard sphere collision theory in which cross sections do not depend on temperature. On the other hand, a large scatter of γ_0 values is observed in the range of 1–3 MHz/Torr, in good agreement with the experimental results of [8].

3.2. Carbon monoxide

Fig. 3 plots the PB parameters for carbon monoxide transitions in the range of 115–576 GHz as functions of temperature in the range of 7–3000 K. In the two upper panels, corresponding to the transitions at 115 and 231 GHz, the RPA results are compared to the measurements and CC calculations of Mengel et al. [4] which cover

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[3] http://www.exomol.com

the range 8–561 K. As in the case of water, we notice that the agreement between the RPA and experimental data improves with temperature: the relative differences are below 10% above 100 K, while they can exceed a factor of 2 below 10 K. Elastic collisions are thus significant below 200 K while above this temperature, the RPA and the CC results converge and agree within about 10%. This 10% difference probably reflects the fact that the CO–H_2 PES employed by Mengel et al. [4] was less accurate than that employed by Yang et al. [24]. A discussion of this can be found in Jankowski and Szalewicz [26]. Thus, the small disagreement between the CC calculations and the experimental points below ~ 40 K, where theory overestimates the broadening, could in fact reflect the inaccuracies in the PES employed by Mengel et al. In this context, we note that a new CO–H_2 PES has been obtained very recently by Jankowski et al. [32]. In the lower panel of Fig. 3, the RPA results are compared with the experimental 576 GHz data of Dick et al. [6]. Agreement is excellent (within error bars) for this transition, suggesting that the RPA is accurate down to about 20 K when CO lies in relatively high lying levels.

As a result, the RPA combined with state-of-the-art inelastic rate coefficients is again found to reproduce the available broadening experimental data within 20% or better above ~ 200 K and at even lower temperature for high lying transitions. In practice, the RPA was employed with the full set of thermalized inelastic rate coefficients computed by Yang et al. [24] (see above), providing broadening parameters for 30 CO transitions in the frequency range 115–3500 GHz, corresponding to energy levels lower than 1700 cm^{-1}, and for temperatures between 200 and 3000 K.

Again, we have fitted our data using Eq. (10) which was found to reproduce our data within 9% or better. The two fitting parameters (γ_0 and β) are provided in Supplementary Tables which are also available on the ExoMol web site. We emphasize that these fits are only valid in the temperature range of $200 \le T \le 3000$ K. It can be noticed from Table S6 [37] that γ_0 lies in the range of 2.6–3.0 MHz/Torr and β in the range of 0.5–0.7.

4. Conclusions

The random phase approximation has been employed to derive the H_2 broadening parameters of water and carbon monoxide from recent state-of-the-art collisional rate coefficients [23,24] at temperatures up to 3000 K. This approximation was compared both to full close-coupling calculations

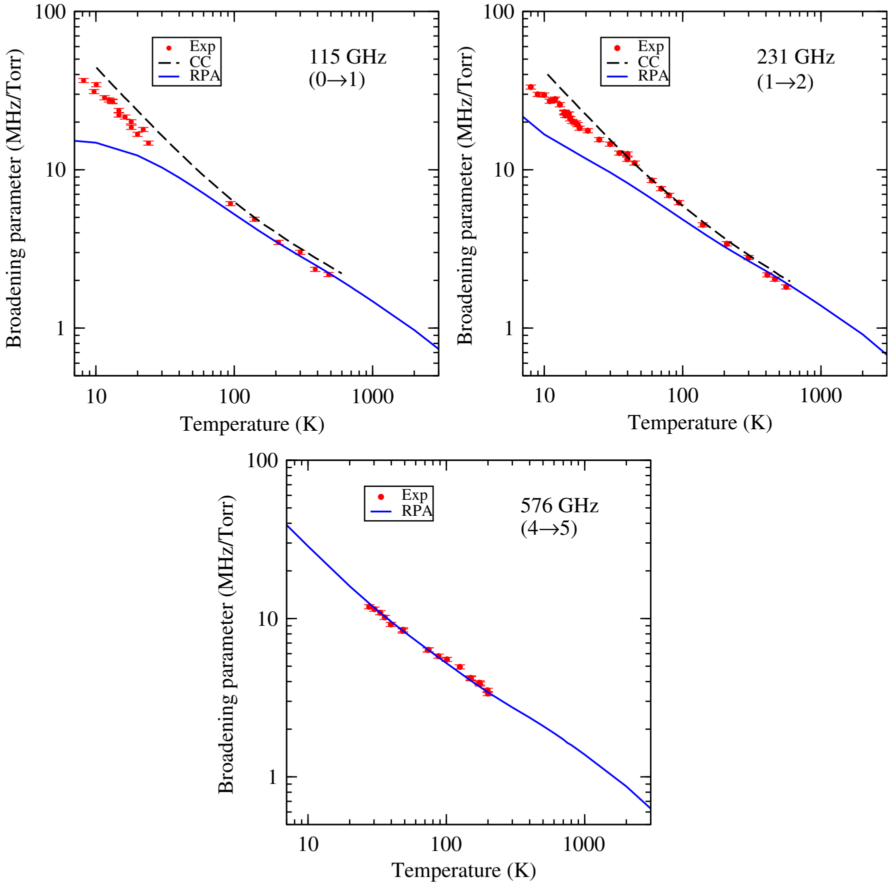

Fig. 3. Broadening parameter (in MHz/Torr) as a function of temperature for three transitions of CO in collision with *n* H_2. The CC calculations (dashed black line) and experimental data (red circles with error bars) at 115 and 231 GHz are taken from Mengel et al. [4]. The experimental data (red circles) at 576 GHz is taken from Dick et al. [6]. The present RPA results are given by the solid blue lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and to available experimental data. It has been shown to be valid at temperatures above ~200 K, as expected from theoretical considerations, with an accuracy of ~25%. It should be noted that for other pertubers, the RPA will hold at lower or higher temperatures, depending on the magnitude of the intermolecular potential well. Thus for He induced broadening, the RPA should be valid down to a few tens of Kelvins while for H_2O induced broadening, the RPA is expected to hold above ~1000 K. This will be quantified in future works.

The present broadening data, combined with the extensive transition frequency and transition intensity data provided by the ExoMol project [16], should help in the modelling of radiative transport properties and spectra of extrasolar planets and cool stars where water and carbon monoxide are abundant. Indeed, they can be used to add pressure dependence to recently derived high-temperature cross sections [33]. The data presented in this work is given in Supplementary Material and on the ExoMol web site (www.exomol.com) from where it will also be integrated into the VAMDC project [34].

We finally note that the current set of transitions covered by our data (i.e. all levels below 1100 cm^{-1} for H_2O and below 1700 cm^{-1} for CO) might prove insufficient for modelling atmospheres with temperatures above ~2000 K. In this regime, rovibrational lines are also important. Future works will concern the extension of the present data to higher J and rovibrational lines.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2012.09.015.

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