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Collisional broadening and hyperfine structure of rotational transitions.

Reply to the comments on
“A never-ending story in the sky:
The secrets of chemical evolution”

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We would like to thank all commentators for their insightful comments, all of them contributing to enrich and complement our review. Among them, the comments by Agúndez - Cernicharo [1], Hochlaf [2], and Feng - Gou [3] provided the opportunity to further extend the discussion.

5 **1. Collisional broadening of the rotational transitions: experimental information on collisional rate coefficients**

The reply “The Place of Quantum Chemistry in Molecular Astrophysics” by Marcellino Agúndez and José Cernicharo [1] reports three interesting examples about the contribution that quantum chemistry can provide to molecular
10 astrophysics, which is how astrophysicists tend to call what chemists define as astrochemistry. The last example concerns the calculation of the rate coefficients for inelastic collisions, the latter being a critical information for deriving molecular abundance from astronomical spectra. This was indeed a topic not

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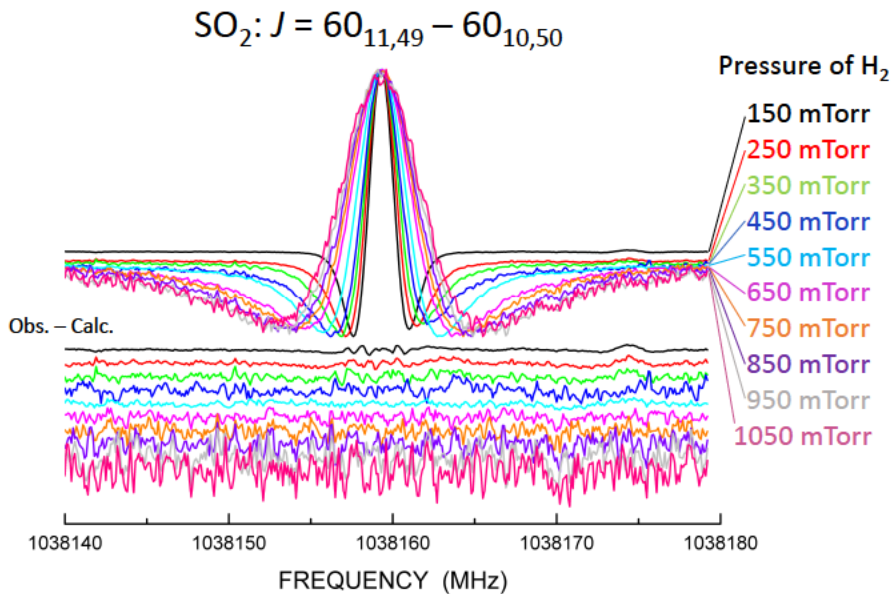


Figure 1: Rotational transition of SO_2 broadened by H_2 : the line profile broadened by increasing quantities of H_2 is shown. The residuals (obs - calc), i.e. the differences between the recorded lines and those calculated with the chosen line profile model, are shown.

touched by our review [4] and, in this respect, we would like to integrate the
 15 theoretical aspects presented by Marcellino Agúndez and José Cernicharo with
 contributions given by experimental rotational spectroscopy.

In addition to the measurements of accurate line positions and their analysis
 in order to provide accurate spectroscopic constants (that in turn can be
 used to accurately predict the rest frequencies of transitions not investigated in
 20 the lab), rotational spectroscopy can also support efficiently collisional dynam-
 ics studies. Indeed, in order to interpret observed interstellar spectra in terms
 of local physical conditions, a knowledge of rates for radiative and collisional
 excitation is needed. Rotational state-to-state collisional rate coefficients are
 thus data of paramount importance for a proper modelling of line observations.
 25 As mentioned in the contribution by Marcellino Agúndez and José Cernicharo,
 the collisional cross-sections and rate constants can be theoretically evaluated

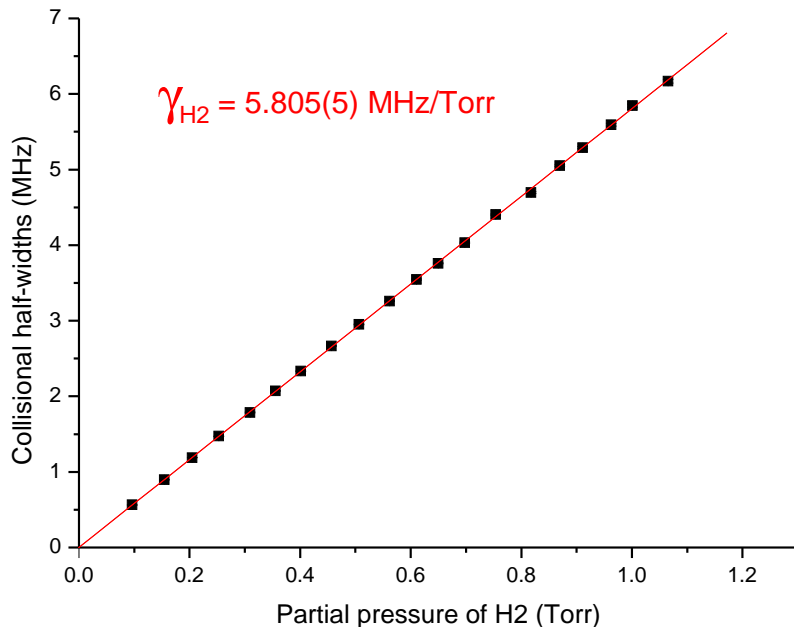


Figure 2: The $J = 34_{11,23} - 34_{10,24}$ rotational transition of SO_2 broadened by H_2 : linear fit of the collisional half-widths versus the partial pressure of H_2 .

[5, 6]. These quantities are expressed in terms of the scattering matrix S , which in turn can be calculated by solving the time-independent Schrödinger equation involving the interaction potential V of the colliding system. Therefore, a high-accuracy potential energy surface (PES) for the interaction between the tracer molecule and a perturber (He or H_2) should be computed. While this aspect is touched later on in the reply to the comment by Majdi Hochlaf [2], here, we address the fact that scattering parameters can be also experimentally derived using the collisional broadening of rotational transitions. Indeed, the line-broadening and line-shift coefficients are related to the real and imaginary parts of the cross-section and of the efficiency function, both derived via the scattering matrix S . The experimental information on the line-widths can

then be obtained by carrying out line measurements in controlled pressure and temperature conditions, i.e. by performing pressure broadening measurements. Although these studies can not directly estimate state-to-state rates, they provide an important experimental validation of the computational procedure. In fact, the parameters derived by line-profile studies represent not only a stringent test for the accuracy of the PES used in the scattering calculations, but they also provide a mean to improve the theoretically computed potential by morphing it to fit the experimental data [7].

The experimental procedure is rather simple: a rotational transition or a portion of spectrum of the tracer molecule is recorded at low pressure; then, the selected line or the collection of transitions are recorded at increasing quantities of the perturber. The line profiles of the recorded spectra are analyzed in order to retrieve the corresponding line widths and the line shifts. The model to be used in this analysis is a critical issue, see –for example– ref. [8] and references therein. The pressure broadening (or shift) coefficients are then determined by linear fits of the retrieved line widths (or shifts) versus the perturber pressure values. An example of line profile analysis is shown in Figure 1, while Figure 2 depicts an example of the linear fit mentioned above. Both examples considers SO_2 as the tracer and H_2 as the perturber. Data are taken from ref. [9].

2. Non-reactive potential energy surfaces: Effective yet accurate energetics and modeling

In the comment “In-silico astrochemistry of life’s building blocks” by Majdi Hochlaf [2], an interesting (and important at the same time) point has been mentioned, which has not been addressed in our review [4]: the derivation of the molecular abundances from astronomical spectra also requires the collisional rates of the molecules of interest (i.e. the tracers) with the most abundant perturbing species, namely H_2 and He [6]. At the basis of the evaluation of the collisional rates, there is the quantum-chemical calculation of the multi-dimensional potential energy surface (PES) for the tracer-perturber interacting system. In

ref. [2], the good performance of explicitly correlated coupled-cluster methods for the generation of such potentials is assessed [10, 11]. In particular, in refs. [10, 11], it was pointed out that the CCSD(T)-F12/aug-cc-pVTZ level of theory [12, 13, 14, 15] is suitable for the correct description of the critical regions of the PES and that diffuse functions are crucial for that purpose, the *cc-pVnZ-F12* (with $n = D, T$) basis sets being not adequate. Similar conclusions on the need of incorporating diffuse functions for quantitative results were obtained for intermolecular complexes in ref. [16], where the jun-ChS composite scheme was introduced and validated. This modified version of the “cheap” composite scheme [17, 18] shows a very good compromise between accuracy and computational cost. The jun-ChS model starts from the CCSD(T)/jun-cc-pVTZ level of theory [19, 20] and accounts for the contributions of the extrapolation to the complete basis set limit and of the correlation of core electrons at the MP2 level [21]. Since the computational bottleneck is the CCSD(T) calculation and the jun-cc-pVTZ basis set is by far smaller than the aug-cc-pVTZ set, the jun-ChS scheme might offer an improved alternative to the CCSD(T)-F12/aug-cc-pVTZ level of theory for the evaluation of the multi-dimensional PESs required for deriving collisional rate coefficients. Nevertheless, the role of diffuse functions on H (in H₂) and He must be investigated in more details.

Similar issues arise in the calculation of the rate constants for barrierless elementary reactions, which often rule the entrance channels of radical-neutral reactions occurring in the ISM. However, the dimension of the involved systems and the number of different reactions to be considered require the use of more approximated models, where an effective radial potential is obtained from the proper averaging of the non-isotropic components of the interaction energy. The simplest approach of this kind is the phase space theory (PST) [22, 23], which leads to an analytical expression for the microcanonical or canonical rate constant under the assumption that the effective potential can be fitted by a Lennard-Jones function [24]. This model is applicable only if the dynamical bottleneck of the entrance channel occurs at large separations, where the interacting fragments have free rotations and unperturbed vibrations. Such an

assumption is generally valid for low-temperature phenomena, as those occurring in the ISM. Despite its simplicity, PST often leads to rate constant within a factor of two from accurate results, this accuracy being comparable to that issuing from accurate electronic structure computations [25]. Examples of successful application of PST in conjunction with transition state theory for reaction steps ruled by potential barriers are provided by the formation of formamide in cold interstellar clouds [26], the gas-phase formation of glycolaldehyde, acetic acid, and formic acid [27], as well as an ongoing study concerning the reaction of the CN radical with methylamine.

3. The role of hyperfine structures in astronomical spectra

An interesting point raised by the comment “Possibilities and challenges in astrochemistry: Computational and spectroscopic strategies” by Gang Feng and Qian Gou [3] concerns the fact that the pattern of the hyperfine structure of rotational transitions might help in the assignment of astronomical observed spectra. In our review [4], the quantum-chemical aspects of rotational spectroscopy have been addressed, but no mention has been done on the hyperfine structure. While it has been pointed out that even state-of-the-art quantum chemistry is not able to provide predictions of rotational frequencies sufficiently accurate for guiding astronomical searches (see also refs. [28, 29]), different is the situation for the hyperfine parameters, for which quantitative estimates can be obtained (see, e.g., refs. [30, 31]). A significant example in this respect is provided by the investigation of the hyperfine structure in the rotational spectrum of CF^+ reported in ref. [32]. In that work, the spin-rotation interaction constant was accurately computed and allowed to explain (and perfectly reproduce) the double-peaked feature in the astronomical observation of the $J = 1 - 0$ transition. The role played by quantum chemistry was fundamental because the spectroscopic study of CF^+ was not able to resolve the hyperfine components in the rotational spectrum [33]; indeed, for ionic species –produced on-the-fly by DC discharge– standard rotational spectroscopy techniques are not able to

exploit the required sub-Doppler resolution.

Hyperfine structures of rotational transitions play an important role because an error in the line width is transferred to the column density estimate. This
130 has been clearly pointed out in the recent investigation of the NH₂D hyperfine structure revealed by astrophysical observations [34]. The authors found that when the hyperfine splitting due to the D nucleus is neglected, the line analysis leads to overestimating the line widths of the *o/p*-NH₂D lines, with the error for a cold molecular core being as large as 50%. However, the work reported in ref.
135 [34] only provided an incomplete determination of the hyperfine parameters, which have been exhaustively derived in a very recent spectroscopic work [35]. Even if the hyperfine structure is not resolved in the astronomical features, for correctly retrieving their column density, it might be fundamental to take it into account, as pointed out in ref. [31].

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