Rates of conversions of molecular internal energy to and from kinetic energy by means of molecular collision allows to compute collisional line shapes and transport properties of gases. Knowledge of ro-vibrational quenching rates is necessary to connect spectral observations to physical properties of warm astrophysical gasses, including exo-atmospheres. For a system of paramount importance in this context, the vibrational bending mode quenching of H$_2$O by H$_2$, we show here that exchange of vibrational to rotational and kinetic energy remains a quantum process, despite the large numbers of quantum levels involved and the large vibrational energy transfer. The excitation of the quantized rotor of the projectile is by far the most effective ro-vibrational quenching path of water. To do so, we use a fully quantum first principle computation, potential and dynamics, converging it at all stages, in a full coupled channel formalisms. We present here rates for the quenching of the first bending mode of ortho-H$_2$O by ortho H$_2$, up to 500 K, in a fully converged coupled channels formalism.
Collisional exchange of energy (internal and kinetic) is a fundamental process leading to the equilibrium between internal temperatures of molecules and kinetic temperature of the gas in which they are immersed. There exists many attempts to compute those rates for transport properties, all the way from classical computation (recent examples are) to full quantum ab initio computations. While a large body of investigation deals with collisional rates for astrophysics and planetary science, as described in the next paragraph, the role of internal to kinetic energy exchanges is also crucial in cold molecules physics ($T \sim K$ to $mK$). In an cold molecular gas, energy exchanges between the molecules observed and with the buffer gas, possibly causing heating of the cold molecules.

The recent surge in interest towards elastic and inelastic collisions stems mainly from precise atmospheric/astrochemical needs. Most data pertaining to the physical and chemical-physical states of gaseous matter in the Universe come from atomic or molecular spectroscopy. For decades, most of the quantitative information was gained from the rotational lines of ground state molecules, thanks to the high precision, high specificity of rotational spectra in the cm to sub-mm spectral regions.

Because of newer instruments on the ground and thanks to plane- or space-born telescopes, the opacity of the atmosphere to FIR-IR light is progressively overcome, and opens up new opportunities: Microwave (THz frequencies) to Infra Red spectra carry information otherwise unattainable, on the warm interstellar matter and on planetary/cometary atmospheres in the Solar System or in exoplanets. Many molecules are thus nowadays observed in their vibrationally excited states, whether by rotational spectroscopy within those states, or else by observing the FIR-IR lines connecting different ro-vibrational levels. Among the molecules observed, water is prominent, being the third most abundant (after $H_2$ and CO) and the first polyatomic one. The relevance of the ro-vibrational quenching of water is further enhanced by the relatively recent discovery of masing transition of ortho-water, in the transition $v_b = 1; 1_{10} \rightarrow 1_{01}$, at $\nu = 658.00$ GHz [Rotational levels of water are labelled $j_{k_a k_c}$; ortho $^1$H$_2$O (nuclear spin triplet) has $k_a + k_c$ odd; $v_b$ is the water bending mode quantum number].

The present approach constitutes, for the author’s best knowledge, a first *ab initio* study of quantum ro-vibrational quenching for a polyatomic molecule, that includes rotational states of the projectile. Integrating these new rotational channels increases the magnitude of the vibrational quenching rates (and cross sections) by several orders of magnitude, when compared with earlier work, either classical or quantum. It has always been expected that quantum effects would
dominate the landscape for low collisional energies, comparable to the minimum of the van der Waals potential $|V_{\text{min}}|$ (here, $V_{\text{min}} \approx -250 \text{ cm}^{-1}$)\textsuperscript{20–22}, but quantum aspects are supposed to disappear progressively as the collision energy increases. In a very different context, combustion modelling\textsuperscript{3}, the same assumption is made that there exists a critical temperature $T^* = kT/|V_{\text{min}}|$, above which classical picture is sufficient to describe collisional transport.

We show here that the very different energy scales of water rotations, molecular hydrogen rotation, and water vibration lead to the resurgence of a strong dependence of the cross sections to the quantum levels of H$_2$ and H$_2$O involved. This resurgence does not happen for purely rotational energy redistribution: even classical and/or statistical approaches\textsuperscript{23} are relevant when a large number of coupled levels interact. It is most significant here, and, to a lesser extent, to collisions involving water and a heavier partner, like N$_2$, which is described by a toy model in this work.

While classical and semi-classical methods are certainly of relevance in rotational quenching, it must be recalled that the semi-classical quantization of an asymmetric rotor is problematic\textsuperscript{24}, at least for $j$ small enough so that the two associated levels $j_{k_a,k_c}$ and $j_{k_a-1,k_c+1}$ are clearly distinct.

Computing collisional coefficients for purely rotational transitions has been a nearly continuous endeavour since the pioneering work of Delgarno\textsuperscript{25–32}. The scenario is always the same, and it is the one we pursue here: (i) Computing \textit{ab initio} the interaction potential $V_n(R)$ of the polar molecule and the projectile ($R$ denotes collectively all necessary coordinates, $n$ are the points where computing is performed), (ii) fitting the $n$ computed points onto a functional form acceptable for dynamics, (iii) running quantum dynamics of the collision pair, and (iv) computing cross-section as a function of collisional energy $\sigma(E)$ or rates as a function of the kinetic temperature of the collider gas $k(T)$.

Thanks to the experience gained in recent precise rotational inelastic scattering computations and of very convincing comparisons of theory with several types of experiments\textsuperscript{20,22,33}, it is safe to deal with ro-vibrational collisional excitation with the same types of methods and basis sets that were used previously, and conduct a fully quantum dynamical approach.

We employ the full dimensional (9 degrees of freedom) water-molecular hydrogen potential energy surface\textsuperscript{34} (hereafter denoted val08), $V(R, \Omega, \delta r_q)$. This surface includes the 5 intermolecular degrees of freedom (intermolecular distance $R$ and 4 angles $\Omega$ to orient one molecule with respect to the other), as well as 4 normal coordinates describing motion around equilibrium position of the molecules, $\delta r_q$, $q = 1, \ldots, 4$. Details of this surface are in the original paper. Since quantum
dynamics is performed with a quantum time-independent computation of the S-matrix, we need to fit the ab initio points on the relevant S. Green type of mixed coordinates\textsuperscript{28}. Molscat code was used\textsuperscript{31}, duly modified to include vibrational modes in the potential expression. We did not include the modification of the kinetic energy due to rovibrational motion\textsuperscript{35}, but restricted ourselves to potential effects, and expressed the potential in coordinates satisfying Eckart conditions. Since we deal only with the first bending mode \( v_b = 1 \) and low lying rotational levels in the excited vibrational mode, we made the assumption: \( |v_b; j_{k_a,k_c}\rangle = |v_b\rangle \otimes |j_{k_a,k_c}\rangle_{v_b} \). The rotational functions are parameterized by the rotational parameters of either \( v_b = 0 \) or \( v_b = 1 \), but they are not rovibrational functions. We also averaged the dependance of the potential on the vibrational ground state of \( \text{H}_2 \).

Time-independent quantum dynamics is performed here on two coupled sets of potential energy surfaces with full dimensional (5D) potentials, including \( \text{H}_2 \) rotation (denoted by the quantum number \( j_2 \)), in a converged coupled channels approach. The potentials were obtained by computing the averages of the 9-D potential: \( C_{v'_b,v_b}(R,\Omega) = \langle v'_b|V(R,\Omega,\delta r_q)|v_b\rangle \) functions, with \( v'_b, v'_b = 0, 1 \) [see val08]. The coupling \( W(R) \) matrix is thus written blockwise as (with \( R \) the intermolecular distance)\textsuperscript{37}.

\[
\Psi''(R) = \left[ \begin{array}{c} W_{11}(R) & V_{01}(R) \\ V_{01}(R) & W_{00}(R) \end{array} \right] - \frac{\ell^2_2}{\ell^2_1} \Psi'(r) \tag{1}
\]

where the \( W_{00}(R) \) and \( W_{11}(r) \) matrices are formed by using the potential of each vibrational level (including the diagonal contributions), and the non-diagonal rotational terms, bracketed with the relevant spherical harmonic functions\textsuperscript{28}[val08]. The \( V_{01}(R) \) matrix is also given by duly bracketing the \( C_{v'_b,v_b}(R,\Omega) \) function with the same spherical harmonic functions.

In order to be able to deal with representative (symmetric) matrices of sizes less than 12,000 \( \times \) 12,000 (the practical limit of OpenMP computing), we further split the computation by treating each total angular momentum value \( J \) (recoupling \( j, j_2, \ell \), the orbital angular momentum) and, if necessary, each inversion symmetry, separately. We used a relatively coarse grid of total energies (\( E_{\text{tot}} \) from threshold to about 3,000 cm\(^{-1}\)), as we are not interested in the detailed resonance behaviour occurring typically at 1 cm\(^{-1}\) < \( E_{\text{collison}} \) < \( |V_{\text{min}}| \).

We present results for ortho \( ^1\text{H}_2\text{O} \) - ortho \( ^1\text{H}_2 \) collisions. The present analysis could serve as a basis for the modelling the masing transition of water at 658 GHz\textsuperscript{14,38}; also, ortho \( \text{H}_2 \) is more abundant than para \( \text{H}_2 \) at the higher temperatures that we examine. With a large rotational basis set we computed all inelastic cross sections with initial levels \( v_b = 1; j_{k_a,k_c} = 1_{01} \) up to \( 3_{21} \). Rotational
basis for water is \( j(v = 0) \leq 14; j(v = 1) \leq 6 \); only rotational levels with \( E \leq 3500 \text{ cm}^{-1} \) are included. Convergence was reached at higher energies for total angular momentum \( J = 28 \) to 32.

Next (Fig. I), we compute quenching cross sections as a function of scattering energy and quenching rates as a function of temperature (inset of Fig. I). In both figures, we show the total quenching section (or rate) from a series of excited ro-vibrational levels (as described in the caption of Fig. 1) to all \( \nu_b = 0 \) levels and constraining to de-excitation (Excluding the \( \nu_b = 0 \) levels that are above the \( \nu_b' = 1 \) original levels):

\[
\sigma_{\nu'=0 \leftrightarrow \nu=1,j_{k_a}k_c} (E) = \sum_{j', k'_a, k'_c} \sigma_{\nu'=0,j'_{k'_a}k'_c \leftrightarrow \nu=1,j_{k_a}k_c} (E),
\]

and rates obtained therefrom by averaging over the collisional energy. Fig. I shows results for three rotational bases of the \( \text{H}_2 \): (i) para-\( \text{H}_2 \), \( j_2 = 0 \), to be compared with the results of \( ^{18} \) (ii) \( j_2 = 1 \), the usual basis for many computations for collisions between a molecule and ortho-\( \text{H}_2 \), (iii) a larger basis for ortho-\( \text{H}_2 \), \( j_2 = 1, 3 \). Full results with all detailed cross sections and rates will be published elsewhere.

![Fig. 1](image.png)

**FIG. 1.** Left panel: Quenching cross section (log scale) as a function of collision energy. Individual transitions denoted by colors and line types. Right panel: corresponding rates \( k(T) \). Colors of the lines designate the original \( \nu = 1 \) rotational level. Line types designate the rotational basis of \( \text{H}_2 \): Lower group: \( \sigma^0(E) \); middle group, \( \sigma^1(E) \), upper group \( \sigma^{13}(E) \), see text.
Results are striking, as the main channel of quenching appears to go via a simultaneous ro-vibration quenching of $\text{H}_2\text{O}$ and a rotational excitation of $\text{H}_2$, from $j_2 = 1$ upwards to $j_2 = 3$, an excitation of about 600 cm$^{-1}$ (to be compared with a vibrational threshold at 1585 cm$^{-1}$), Fig. 1. Note that the $j_2 = 5$ level has an excitation threshold at 1620 cm$^{-1}$, above the $j_2 = 1$ levels. We made some preliminary computations of the influence of the full $j_2 = 1, 3, 5$ basis. The increase at a collisional energy of about 1500 cm$^{-1}$ is of the order of 15%. Full investigation will be presented in future papers. The relevance of the $\Delta j_2 = +4$ is marginal at the energies considered here.

Cross sections are very significantly larger for collisions with ortho-$\text{H}_2$ than with para-$\text{H}_2$, $j_2 = 0$, an expected result, due to the non isotropy of $\text{H}_2$ (static quadrupole and anisotropic polarizability of $\text{H}_2$, allowing for anisotropic long-distance interaction). The effect is particularly large, but remains compatible with other collisions with a polar molecule$^{39–41}$. Here, however, vibrational quenching cross sections gain another order of magnitude with including both $j_2 = 1$ and $j_2 = 3$ ortho rotational levels of $\text{H}_2$, remaining with initial conditions at $j_2 = 1$. An earlier classical work$^{35}$ did not see such a strong effect at all (see their figure 4, with a monotonous decrease of rotational energy of $\text{H}_2$ after collision). The recent quantum paper$^{18}$ did not consider these possibilities. Some hints of the importance of the rotational transitions of the projectile are seen in$^{42}$.

Before trying to interpret the surprising results of Fig. 1 let us compare those results with previous work. We compared present rate results with earlier ones by Daniel et al.$^{43,44}$, for pure rational quenching inside the $v_b = 0$ levels, for temperatures up to 500 K, see Fig. 2. Agreement is not perfect, as expected, since Daniel et al. had a different definitions of rates and convergence (including the $j_2 > 0$ channels in their initial conditions), unrealistic for the computations here, but the important features are present, validating the code and the method.

The $j_2 = 0$ cross sections found here (lower manifold of Fig. 1) is readily found to be comparable in magnitude to those found by Stoecklin et al.$^{18}$. Secondly, in$^{45}$, a large set of transitions and temperatures was proposed, based on classical and statistical assumptions. It is difficult to compare their results with the ones presented here, as their methodology is more suited for higher $T$, higher initial $j$ and makes no assumption on ortho or para state of $\text{H}_2$. To work qualitatively, at 300 K, we find a total rate $k(300 \text{ K}) = 3.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ (summed over all initial levels considered, $1 \leq j \leq 3$) and their rates amounts to $9.7 \times 10^{-12}$ approximately, as taken from the LAMDA database, https://home.strw.leidenuniv.nl/ moldata/ (also summed on all initial levels, $j \leq 3$). Experiment points to $1.3 \times 10^{-12}$, with no very clear definition of the
FIG. 2. Rates of de-excitation of ortho-H$_2$O levels in $v_b = 0$, by ortho-H$_2$. Diamonds, Daniel et al.$^{43}$; line, this work.

initial state.$^{46}$ Clearly, the experiment-theory comparison must be made more precise, probably by examining pressure broadening of IR/Raman spectroscopy.

The magnitude of the rates allow us to infer the critical densities. Allowed water IR transitions are the following: $\Delta v_b = \pm 1; \Delta j = 0, \pm 1,$ and $\Delta k_a + \Delta k_c = 0, \pm 2$. IR transitions of the low $j, v_b = 1$ occur at larger IR frequencies, hence, a relatively large average spontaneous emission rate $A = 24.6 \text{ sec}^{-1}.^{47}$ Critical densities of H$_2$ are thus of the order of $n^* = 7 \times 10^{12} \text{ cm}^{-3}$, well within the range of atmospheric densities and outflows of aging stars. Please note that critical densities (as well as rates) are not unambiguously defined here, as many temperatures may coexist. We made use of one kinetic temperature for H$_2$, and summed over all quenching rates.

To disentangle various possible effects leading to the results of just outlined, we devised four different scenarios for total quenching cross sections $\sigma \equiv \sigma(v'_b = 0 \leftrightarrow v_b = 1)$, summed for all final rotational levels. They differ by the H$_2$ rotational bases and the way to treat the rotational excitation of H$_2$: (i) $\sigma^0(j_2 = 0)$, (ii) $\sigma^1(j_2 = 1)$, (iii) $\sigma^{13*}(j_2 = 1, 3)$, but forbidding the $\Delta j_2 = \pm 2$ transitions, and (iv) $\sigma^{13}(j_2 = 1, 3)$, allowing for $\Delta j_2 = \pm 2$ transitions. They all are shown in Fig. We see that the $\sigma^1$ and $\sigma^{13*}$ cases are very similar, with an order of magnitude difference with $\sigma^0$ and $\sigma^{13}$ To understand the dynamics at hand, we took a twofold approach.

**Firstly**, we compared, for similar quenching energies, the $\Delta j_2 = 0$ ($\sigma^{13*}$) to the $\Delta j_2 = \pm 2$ ($\sigma^{13}$), for ro-vibrational quenching or pure rotational quenching (Fig. 3). We present results summed over all partial waves (total angular momentum), either as a function of the total collision energies.
(panels (a) and (c)) or as a function of the final rotational state \( j \) of (panels(b) and (d)). Initial conditions are chosen as follows: For panels (a) and (b), initial states are \( v = 1, j_1 = 1, 2, j_2 = 0 \), that is initial total energy \( 1737.2 < E < 1861.5 \text{ cm}^{-1} \). For panels (c) and (d), we take initial levels at \( v = 0 \), total \( 1737.2 < E < 1900 \text{ cm}^{-1} \), and \( 9 \leq j \leq 11 \). In this way, energy gap effects are kept more or less the same, whether with or without vibrational quenching.

Examining the results, for panels (a) and (b) - vibrational quenching-, we see that initial collisional energy has no peculiar feature and that final water angular momentum is weakly peaked at \( j \sim 6, 7 \), for both final \( j_2 = 0, 2 \). For panels (c) and (d) -no vibrational quenching-, initial collisional energy peaks at about \( 1300 \text{ cm}^{-1} \) and diminishes strongly for smaller values. There is a propensity towards \( \Delta j_2 = +2 \) for small final \( j \) (large \( \Delta j < 0 \)) and the opposite for larger final \( j \). This goes in favour of a split of outgoing angular momentum between the two outgoing products, not seen in vibrational quenching.

The \( \Delta j_2 = +2 \) channel dominates the picture for vibrational quenching by at least one order of magnitude when the channels are opened (right of blue threshold line, panels (a), (c), \( j \leq 10 \), panels (b),(d)). It is not the case for pure rotational quenching. It is all the more remarkable that for the \( v = 0 \rightarrow 0 \) quenchings, the loss of angular momentum is much higher, with \( j_{\text{ini}} \geq 9 \). \( \text{H}_2 \) carrying away angular momentum is not the main effect here. Also, energy loss is similar, hence energy gap effects are ruled out in the comparison. Inside the \( v_b = 0 \) vibrational level, we find a weak dominance of the \( \Delta j_2 = 0 \) transitions, similar to what Daniel et al. found (Figure 1 of reference Daniel et al.\textsuperscript{40})

Secondly, we compute and draw the ro-vibrational channels that are used for the dynamical propagation, as a function of \( R \). We consider the diagonal part of the \( W(R) \) matrix (equation\textsuperscript{41}) as a diabatic image and its eigenvalues, eig [\( W(R) \)] as an adiabatic image, Fig. \textsuperscript{4}. Plots are for total \( J = 2, j \leq 3 \), a good compromise between generality (the \( J = 6 \) or 12 are very similar in appearance; adding \( j \) channels do not change the picture) and as small a number of channels as possible, for sake of readability. We see straightforwardly that in the case of \( j_2 = 0 \), crossings between incoming black \( v_b = 1, j_2 = 0 \) channels and outgoing red \( v_b = 0, j_b = 0 \) channels are limited to the repulsive wall, at very high collision energies. Cross sections are exceedingly small, but increase rapidly once the crossings are open, energy-wise. Exchanges between the various \( v_b = 0 \) channels is possible, seemingly at all energies and distances. The \( j_2 = 1 \) case does not fundamentally change the picture. There are crossings (diabatic picture) or avoided crossings for energies lower than threshold, at \( R \sim 8 \text{ Bohr} \), sufficiently effective to insure some transfer.
FIG. 3. Comparison between rotational quenching, for transition without excitation of H$_2$ ($\Delta j_2 = 0$, black bars), and with excitation of H$_2$ ($\Delta j_2 = +2$, red bars). Total angular momentum summed, $0 \leq J \leq 32$. Panels (a), (c), cross sections as a function of collision energy. Blue vertical line indicate the $\Delta j_2 = +2$ threshold. Panels (b), (d), cross sections as a function of final H$_2$O principal rotation quantum number $j$. $j = 11, 12$ are above threshold for $\Delta j_2 = +2$ excitation. Panels (a), (b), rovibrational quenching (summed for all initial $v_b = 1, j \leq 2$ and all final $v_b = 0$, $E_i > E_f$). Panels (c), (d), pure rotational quenching (summed for all initial $v_b = 0, E \geq 1585$ cm$^{-1}$ and all final $v_b = 0$, $E_i > E_f$). Last bars in panels (b), (d) sum all contributions.

of probability amplitude. Note that the higher energy, $R \sim 10$ avoided crossings should be less efficient, in a Landau-Zener picture, because of the large slope difference between the adiabats.

Picture changes dramatically for the third case, $j = 1, 3$, $\Delta j_2 = 0, +2$, two lower panels. If we detail the diabatic picture (lower left panel), we see (i) that the $v_b = 1, j_2 = 1$ channels (black) are allowed to cross the $v_b = 1, j_2 = 3$ channels (green) in the $R \sim 10$ region, allowed energy-wise. Then, (ii), the probability amplitude, divided into many channels, crosses a large manifold of
$v_b = 0, j_2 = 3$ (magenta) or $v_b = 0, j_2 = 1$ (red) channels, at $R \sim 7 - 10$, in the diabatic picture, allowing for probability amplitude to flow out on the whole manifold. This picture accounts for the increase of inelastic cross sections and rates, but without any propensity rule apparent. If we turn to the adiabatic picture (lower right panel), we see that the magenta levels have a series of avoided crossings with the incoming channels at all distances. The larger number of magenta adiabats, their avoided crossings at all distances, including the larger $R$ distances just below threshold may be enough to point to the propensity rules observed in the quantum dynamics.

To conclude the discussion, we found it worthwhile to have a first glimpse of what the situation might be, for a heavy-heavy collision of utmost atmospheric importance, H$_2$O···N$_2$. Even if a very recent rigid bender PES exists, fits are not in line of what is needed here, and we look only fore some very qualitative results. We used the same PES as before (same symmetry of the system); it is all the more justified that $V_{\text{min}}$ remains similar (about 250-300 cm$^{-1}$). This tN2 (toy-N$_2$) computation of diabats and adiabats is performed exactly similarly, with the two following changes: $B_{N_2} = 2.01$ cm$^{-1}$ and reduced mass $\mu = 10.9565$. While ortho and para $^{14}$N$_2$ have the opposite meaning from $^1$H$_2$ (because of the bosonic character of $^{14}$N, of nuclear spin $I = 1$), we did not change the $j_2$ values.

Fig. 5 show the results, with the same conventions as in Fig. 4. Without any supposition for the dynamics, we see that the same effects persist, namely, a large increase of avoided crossings, from $j_2 = 1$ to $j_2 = 1, 3$. In this tN2 case we have a large decrease (factor of 25) of the projectile rotational constant (here below the target rotational constants), but the vibrational gap remains. The large fans of adiabats should allow for higher cross sections, because of the various energy scales involved.

One should not take those tN2 computations for more than indications. In particular, they do not claim for any convergence. However, they should be a warning before deciding whether a cold molecule collision vibrational quenching proceeds classically for all the energy sectors considered. In low $T$ physics, it could be fine structure, vibration, rotation, and each could operate in a very different way.

Foseca dos Santos et al. studied some time ago the H$_2$···H$_2$ system, considering ro-vibrational de-excitation cross sections, for both ortho-para and ortho-ortho collisions, at mostly low collisions energy (up to 100 K). Since in the present work, molecules are distinguishable, the comparison is more relevant in the ortho-H$_2$···para-H$_2$ case, as the ortho-ortho case presents resonances and symmetry effects absent here. We found here that the dominant channel for vibrational quenching
FIG. 4. Diabats and adiabats for the H$_2$O···H$_2$ collision. Left panels, diabats (diagonal part of the W matrix, Eq. (11)), as a function of intermolecular distance. Right panels, adiabats (eigenvalues of the W matrix, Eq. (11)) as a function of intermolecular distance. Asymptotic quantum numbers: black lines: $v_b = 1$, $j_2 = 0$ or $j_2 = 1$; red lines $v_b = 0$, $j_2 = 0$ or $j_2 = 1$; light green $v_b = 1$, $j_2 = 3$; magenta $v_b = 1$, $j_2 = 1$. Blue dashed line: $v_b = 1$, ortho H$_2$O threshold. See discussion in the text.
FIG. 5. Diabats and adiabats for the H₂O···tN₂ collision. Left panels, diabats (diagonal part of the W matrix, Eq.(1)), as a function of intermolecular distance. Right panels, adiabats (eigenvalues of the W matrix, Eq.(1)) as a function of intermolecular distance. Asymptotic quantum numbers: black lines: ν_b = 1, j_2 = 0 or j_2 = 1; red lines ν_b = 0, j_2 = 0 or j_2 = 1; light green ν_b = 1, j_2 = 3; magenta ν_b = 1, j_2 = 1. Blue dashed line: ν_b = 1, ortho H₂O threshold. See discussion in the text.

is j_2 = 1 → 3, irrespective of the collision energy (Fig. 1), thereby reducing the amount of energy to be transferred, independently of angular momentum transfer. The situation is somewhat different for H₂···H₂: for the 1001 collision, (notation:ν_1j_1ν_2j_2; 1,2 the two H₂ molecules), the dominant channel by far is 1001 → 0011, conserving the rotational angular momentum. The analogous 1001 → 0201 is about a factor 5 smaller. An adiabatic analysis similar would sort out the differences, that may be due to the paucity of adiabatic levels (two rods, B = 60 cm⁻¹, far fewer channels). The ortho-ortho case is quite different from the case analyzed here, as resonances and symmetry effects may be dominant effects.
We have shown that the vibrational quenching behaves in a very different way than the rotational quenching, because of the organization of the ro-vibrational quantum levels. Approximations not allowing rotational (and possibly vibrational) excitation of the projectile may be underestimating the actual rates by a large amount, here by a factor of 10 at least. Ignoring the nuclear symmetry of the projectile would also lead to large over-estimation of rates. The results presented here suggest that ro-vibrational quenching by light atoms or by molecules at their zero angular momentum level is fundamentally different from non-zero angular momentum, because both long distance and short distance behaviours of the diabatic or adiabatic channels.

The atmospheric vibrational quenching, driving the IR radiation redistribution towards kinetic energy should thus be carefully conducted in a manner allowing for all the essential angular momenta to be properly taken into account. Probing line shapes via IR/Raman spectroscopy is all the more relevant and will be the object of further theoretical investigations. The critical density found for ro-vibrational quenching points to high atmospheres of stars or planets, to dense parts of late stage stars, confirming that the 658 GHz maser line finds its origin in the unbalance of collisions and optical rates for the low \( j, v_b = 1 \) levels.

As the similarity of rates for the various initial states in our limited range of initial water angular momentum suggests, it is worthwhile to develop specific ways of treating theoretically ro-vibrational quenching, as was done long ago for rotational quenching, to ease the burden of computation time. In this way, the all-important collision systems for our atmosphere (\( \text{H}_2\text{O}/\text{CO}_2/\text{CH}_4 \cdots \text{N}_2/\text{O}_2 \)) will become doable by relevant quantum methods.

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DATA AVAILABILITY

The potential energy surface has been published earlier. The Fortran subroutines for computing the full surface are available from the author upon reasonable request. The quenching data presented here are computed from a large body of raw data, which were generated at the CNRS-IDRIS large facility. Derived data supporting the findings of this study are available from the author upon reasonable request.

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