Rotational energy relaxation quantum dynamics of a diatomic molecule in a superfluid helium nanodroplet and study of the hydrogen isotopes case†

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The rotational energy relaxation (RER) of a molecule \( \text{X}_2(j,m) \) in a \( ^4\text{He} \) superfluid nanodroplet [HeND or \( \text{He}(\text{He})_N; \ T = 0.37 \text{ K} \)] has been investigated using a hybrid quantum dynamics approach recently proposed by us. As far as we know, this is the first theoretical study about rotational relaxation inside HeNDs, and here several (real and hypothetical) isotopes of \( \text{H}_2 \) have been examined, in order to analyze the influence of the rotational constant \( B_0 \) of these fast rotors on the dynamics. The structure of the nanodroplet practically does not change during the RER process, which approximately takes place according to a cascade mechanism \( j \rightarrow j - 2; j - 2 \rightarrow j - 4; \ldots; 2 \rightarrow 0 \), and \( m_j \) is conserved. The results are consistent with the very scarce estimated experimental data available. The lifetime of an excited rotational state (\( \approx 10^{-7.6} \text{ ns} \)) increases when: (a) \( B_0 \) increases; (b) \( j \) increases; and (c) \( N \) decreases (above \( N = 100 \) there is a small influence of \( N \) on the lifetime). This also applies to the global relaxation time and transition time. The analysis of the influence of the coupling between the \( j \) and \( j - 2 \) rotational states (due to the \( \text{X}_2 - \text{helium interaction} \) and the \( \text{X}_2 \) angular velocity on the lifetime and related properties has been helpful to better understand the dynamics. In contrast to the RER results, for the vibrational energy relaxation (VER) in HeNDs, when the quantum number \( v \) increases a decrease is observed in the lifetime of the excited vibrational state. This difference can be interpreted taking into account that RER and VER are associated with very different types of motion. Besides, in VER the intermediate excited states show metastability, differing from the RER case. We hope that the present study will encourage more studies to be developed on the RER dynamics in HeNDs, a basic, interesting and difficult to study physical phenomenon about which we still know very little.

1. Introduction

The singular properties of superfluid helium nanodroplets [HeND or \( \text{He}(\text{He})_N; \ T = 0.37 \text{ K} \)] have stimulated a wide range of applications in chemical physics/physical chemistry.\(^1\)–\(^6\) Thus, they play an important role in different situations, such as, \( \text{e.g.} \), high-resolution spectroscopy, the stabilization of metastable species, and the synthesis of metal nanoparticles and nanowires. The superfluidity and the inert chemical character of helium are probably the most relevant characteristics of this quantum solvent in the present context.

Infrared (IR) spectroscopy has been widely applied to determine the influence of HeNDs on the properties of a large and varied number of species (see, \( \text{e.g.} \), ref. 7–35). The quantum solvent induces small vibrational and rotational line shifts and band broadening. The interaction of the solute with the liquid helium is not strong enough to induce vibrational splitting and, therefore, for molecules in HeNDs the vibrational symmetry is not modified with respect to the gas phase (more details on the molecular vibrational dynamics in HeNDs can be found in ref. 36 and in the references cited therein). All the experiments indicated above have been performed in the frequency domain, \( \text{i.e.} \), they are not resolved in time.

Regarding the molecular rotation dynamics in HeNDs, which constitutes the main issue of the present contribution, the effective moment of inertia, the centrifugal distortion constant and estimates of the rotational relaxation time have

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\(^\dagger\) Electronic supplementary information (ESI) available: Time evolution of several properties (\( N = 100 \) unless otherwise indicated). Fig. S1. \( j = 0 \) and \( j = 2 \) populations of \( \text{T}_2 \) from the relaxation dynamics vs. the fitting according to a model. Fig. S2. Expected value of \( \tilde{J} \) for the \( j = 0 \leftrightarrow j = 2 \) relaxation. Fig. S3. Helium radial density for \( \text{T}_2(j = 2) \). Fig. S4. Snapshots of the helium density \( (xy\)-plane) for \( \text{T}_2(j = 2) \). Table S1. Coupling terms squared values, including those of \( \text{T}_2 \) in HeNDs with different \( N \). Fig. S5. Relaxation time properties of \( j = 0 \leftrightarrow j = 2 \) (dependences). Fig. S6. \( \text{T}_2(j = 2) \) relaxation (different properties). Fig. S7. Expected value of \( \tilde{J} \) for several \( \text{Sx}_2 \) relaxations. Fig. S8. Relaxation time properties of \( \text{T}_2(j = 2) \) in HeNDs of different \( N \) (dependences). See DOI: 10.1039/c9cp00952c

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been reported,\textsuperscript{4,7–35} with nearly all of these contributions being of experimental type (IR spectroscopy and a few of them considering the pure rotational spectrum\textsuperscript{14,24} and both the vibrational and pure rotational spectra\textsuperscript{16}). These properties depend significantly on the rotational constant of the molecules and two limit dynamical behaviours have been identified: adiabatic following (heavy rotors) and non-following (light rotors) regimes; where in the last case the movement of the rotor is too fast for the helium to be able to follow it.

The relaxation times of excited rotational states have only been experimentally estimated, based on the comparative analysis of the line widths corresponding to a small number of transitions and assuming the validity of applying the energy-time uncertainty relation \((\Delta E \Delta t \geq \hbar/2)\) as if it were a strict identity. Besides, in the rotational dynamics context mention should also be made of the research carried out on molecular alignment through the use of intense/moderately intense non-resonant lasers.\textsuperscript{37–39} With respect to ordinary (non-quantum) liquids, the experimental information available on the molecular rotational dynamics is also very limited, even though in this case there are a few direct measurements available (cf. Section 3.1).

The theoretical efforts addressed to investigate effective moments of inertia and, in some cases, centrifugal distortion constants have been based on the correlated basis functions-diffusion Monte Carlo (CBF/DMC) method\textsuperscript{10,15,24} and on the diffusion and path integral Monte Carlo method.\textsuperscript{40} Besides, for the rotational alignment analysis the path integral Monte Carlo (PIMC) and the angulon theory methods have been employed.\textsuperscript{38}

Here, we report the first theoretical study of the rotational energy relaxation (RER) of a molecule embedded in a superfluid \(^4\text{He}\) nanodroplet, to the best of our knowledge. To carry out this work, we have used a hybrid quantum dynamics approach recently proposed by us\textsuperscript{36,41} and, as an initial application, we have examined the RER of several isotopes of the \(\text{H}_2\) molecule. These real-time quantum dynamics simulations have been feasible only recently, thanks to the use of the time dependent density functional theory (TDDFT) for the description of superfluid liquid helium (the \(\text{X}_2\) molecule has been described using an ordinary quantum wave function). An analogous/related strategy has been recently employed by our group to investigate the dynamics of other relevant physico-chemical processes involving HeNDs (photo-dissociation of diatomics,\textsuperscript{41–43} atom capture,\textsuperscript{44,45} dimerization reaction,\textsuperscript{46} nanodroplet relaxation,\textsuperscript{47} and vibrational energy relaxation of diatomics\textsuperscript{36}).

The paper is organized as follows. The hybrid theoretical quantum dynamics approach employed is described in Section 2. The most important results obtained for several isotopes of \(\text{H}_2\) and initial rotational excitations are reported and discussed in Section 3. Finally, the summary and conclusions are given in Section 4.

## 2. Theoretical methods

Before describing in detail the theoretical method used for the study of rotational relaxation, it is convenient to make some considerations of fundamental character. Given the complexity of the problem under analysis, a mean field approach has been applied. So, we have the wave function of helium and the wave function of the molecule, and the quantum evolutions of both are coupled through the expected value of the \(\text{X}_2\)–helium interaction potential energy. That is, in this framework we are not taking into account the quantum correlation between the liquid and the rotor. A related approach to the one we apply here was employed to study the solvation of an electron in superfluid helium,\textsuperscript{48} which is a more favourable situation due to the large mass difference between the electron and the He atom (besides, some correlation was included in the electron-helium pseudopotential used).

To describe the quantum correlation, the wave function of the system should be expressed simultaneously in terms of the helium and molecule coordinates, rather than as the product of two functions, one that depends on helium and the other on the molecule. However, the problem posed in this rigorous way is very difficult to solve. An additional difficulty arises from the use of a DFT description (operators are non-linear) for a part of the system (helium) and an ordinary quantum mechanics treatment for the other part (the molecule), which makes it generally not possible to account for quantum correlation (and DFT is the only currently available description for superfluid helium in dynamics studies).

Notwithstanding the previous remarks, there are two important aspects to keep in mind that are specific to the selected systems: (a) the \(\text{H}_2\) molecule and isotopic variants are the fastest molecular rotors and due to this they will move at much higher velocities than liquid helium (except, of course, when the molecules are close to finishing the relaxation to the ground rotational state); (b) the \(\text{H}_2\)–helium interaction is particularly weak compared to the interaction of other molecules with helium. Based on these facts, we believe that, although the quantum correlation is not described, the theoretical approach proposed here is reasonable, at least as a starting point for the study of the complex problem of the rotational relaxation dynamics in superfluid helium nanodroplets.

The rotational relaxation of a homonuclear diatomic molecule, \(\text{X}_2\), in a HeND has been investigated using a hybrid theoretical approach proposed by our group\textsuperscript{36,41} (see below). In this first study the selected molecules are several, real or hypothetical, isotopes of hydrogen in the electronic ground state: \(\text{D}_2\), \(\text{T}_2\), \(\text{Q}_2\), \(\text{Q}_2\) and \(\text{S}_2\); where the last three molecules are hypothetical species with rotational constants \((B_j)\) equal to 1/4, 1/5 and 1/6 of \(B_0(\text{H}_2)\), respectively. We have proceeded in this way in order to analyze the effect of the rotational constant \((i.e., the effect of the mass)\) on the relaxation dynamics. Although some results have been provided on the \(\text{D}_2\) rotational relaxation, the practical difficulties in simulating this relaxation, which is even slower than that of \(\text{D}_2\), have made it impossible for us to carry out its study.

The initial conditions of the dynamics are represented by the helium density of the \(\text{X}_2\) to a particular \((j, m_j)\) excited rotational state, obtained using, \(e.g.,\) Raman techniques. The rotational excitation and global relaxation processes, that happen through
the evaporation of some helium atoms of the nanodroplet, can be represented as

\[ X_0(j = 0, m_j = 0)@(^4\text{He})_N + h\nu \rightarrow [X_0(j, m_j = 0)@(^4\text{He})_N]^* + h\nu' \quad (1a) \]

\[ [X_0(j, m_j = 0)@(^4\text{He})_N]^* \rightarrow [X_0(j = 0, m_j = 0)@(^4\text{He})_N]^* \]

\[ + (N' - N')^4\text{He} \quad (1b) \]

\[ [X_0(j = 0, m_j = 0)@(^4\text{He})_N]^* \rightarrow [X_0(j = 0, m_j = 0)@(^4\text{He})_N]^* \]

\[ + (N' - N')^4\text{He} \quad (1c) \]

where the * symbol indicates that we are considering an excited system, and eqn (1b) and (1c) show that the time required for the \( X_2 \) rotational relaxation doesn’t necessarily have to match with the liquid helium relaxation time (even though for the systems and initial conditions selected the liquid helium is essentially relaxed shortly after the \( X_2 \) rotational relaxation has taken place).

According to the selection rules for pure rotational excitations (rotational Raman), due to the nuclear symmetry (homonuclear diatomic molecules) the resulting state will have \( D(\text{rotational Raman}) = (\text{pure rotational excitations}) \leq 0 \) with respect to the initial state. Hence, these cases are significantly more difficult to describe theoretically than the systems selected here to carry out the first investigation on RER in HeNDs.

In this initial study, in order to avoid additional difficulties, we have described the \( X_2 \) molecule as a rigid rotor, i.e., the vibrational degree of freedom has not been taken into account, and the \( X_2 \) centre of mass (CM) has been fixed at the origin of the coordinates (centre of the doped nanodroplet). Due to the strength of the molecule–helium interaction in comparison to the helium–helium interaction, the optimization of the \( X_0(j = 0, m_j = 0)@(^4\text{He})_N \) nanodroplet leads the diatomics to the center of the nanodroplet in the equilibrium configuration.

The description of the \( X_2 \) CM motion would involve the inclusion of additional and very significant computational difficulties, as three more coordinates should be taken into account. However, here we have considered a reasonable approximation assuming that the \( X_2 \) CM is fixed, due to the following reasons: (a) the liquid helium structure around the \( X_2 \) molecule shows spherical symmetry in the equilibrium configuration (cf. Section 3); and (b) the liquid helium structure during the \( I_2 \) vibrational relaxation practically does not change after the initial excitations and subsequent relaxations, which suggests that in the “softer” conditions associated with the rotational relaxations to be studied an analogous situation would probably occur (in addition, the \( ^4\text{He} \)–\(^4\text{He}\)) interaction energy is about seven times less intense than the \( I_2 \)–\(^4\text{He}\)) one). The structure of the nanodroplet in fact remains essentially unchanged during the rotational relaxation, as it will be confirmed in Section 3.

The RER dynamics has been studied using a ‘divide and conquer’ hybrid approach. Real-time quantum dynamics simulations have been performed combining a commonly used method to describe rather large bosonic systems such as superfluid \(^4\text{He} \) (time dependent density functional theory) and a usual quantum method to account for atoms/molecules in the gas phase (the time dependent wave function) has been applied to describe the \( X_2 \) molecule, including only the rotational degrees of freedom.

The Orsay Trento (OT) phenomenological density functional has been used in the TDDFT calculations, and the non-local contribution to the helium correlation energy and back-flow terms have been neglected for computational reasons, as usual. This strategy allows us to deal with relatively large nanodroplets if needed, so that comparison with experimental results is possible, while keeping a reasonable computational time.

Nowadays, the dynamics study of physico-chemical processes involving HeNDs is only attainable if the superfluid liquid helium is treated by means of the DFT approach, and the OT density functional is the best available one and has been employed in almost all dynamics studies involving superfluid liquid helium. Moreover, when necessary, a modification can be added to the OT density functional to avoid unphysical helium densities that may occur when the interaction between the dopant molecule and helium is strong (e.g., in the case of the interaction of an halogen molecule with helium), a situation that does not correspond to the present case.

The equations of motion for the different degrees of freedom are found by minimising the quantum action (\( A \)):

\[ A[\Psi_{1\text{He}}, \varphi_{X_2}] = \int dt \left\{ E[\Psi_{1\text{He}}, \varphi_{X_2}] - i\hbar \int dR_{1\text{He}} \Psi_{1\text{He}}(R_{1\text{He}}) \frac{\partial}{\partial t} \Psi_{1\text{He}}(R_{1\text{He}}) \right. \]

\[ - i\hbar \int \sin \theta d\theta d\phi \varphi_{X_2}^*(\theta, \phi) \frac{\partial}{\partial \phi} \varphi_{X_2}(\theta, \phi) \right\}, \quad (2) \]

where \( \Psi_{1\text{He}}(R_{1\text{He}}) \) is the complex effective wave function describing the liquid helium, \( E[\Psi_{1\text{He}}, \varphi_{X_2}] = \rho_{1\text{He}}(R_{1\text{He}}) \times \exp[-i\theta(R_{1\text{He}})] \), i.e.,

\[ \Psi_{1\text{He}}(R_{1\text{He}}) = \rho_{1\text{He}}(R_{1\text{He}}) \exp[-i\theta(R_{1\text{He}})] \]

which satisfies the normalization condition \[ \int dR_{1\text{He}} |\Psi_{1\text{He}}(R_{1\text{He}})|^2 = N_i \]

\( \varphi_{X_2}(\theta, \phi) \) is the rotational wave function of the molecule, and \( E \) is the total energy of the system, which is given by

\[ E[\Psi_{1\text{He}}, \varphi_{X_2}] = \frac{\hbar^2}{2m_{1\text{He}}} \int dR_{1\text{He}} |\nabla \Psi_{1\text{He}}(R_{1\text{He}})|^2 \]

\[ + \int dR_{1\text{He}} C[\rho_{1\text{He}}] + \int dR_{1\text{He}} \left[ \sin \theta d\theta d\phi \right] \]

\[ \times V_{\text{He}-X_2}(\theta, \phi, R_{1\text{He}}) \rho_{1\text{He}}(R_{1\text{He}}) |\varphi_{X_2}(\theta, \phi)|^2 \]

\[ - \frac{\hbar^2}{2\rho_{X_2}^2 \cos \theta} \int \sin \theta d\theta d\phi |\varphi_{X_2}(\theta, \phi)|^2 \]

\[ \times \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] |\varphi_{X_2}(\theta, \phi)|^2 \]

\[ (3) \]
where $\mu_{X_2}$ and $r_{eqX_2}$ are the reduced mass and equilibrium distance of the molecule, respectively, and $e_{c}[\rho_{He}]$ corresponds to the potential energy and correlation energy densities of superfluid liquid helium. $V_{He-X_2}(\theta, \phi, R_{He})$ stands for the interaction potential energy between helium and the diatomic molecule, which has been taken from ref. 55 and is based on high level $ab$ initio calculations.

The quantum action described above is minimised by taking variations with respect to each one of the wave functions. This leads to two coupled time dependent Schrödinger-like non-linear equations governing the evolution of helium and the molecule, respectively:

$$\frac{i\hbar}{\partial t} \Psi_{He}(R_{He}) = \left[ \frac{-\hbar^2}{2m_{He}} \nabla^2 + \int \sin \theta d\theta d\phi V_{He-X_2}(\theta, \phi, R_{He}) |\phi_{X_2}(\theta, \phi)|^2 + \frac{\delta_{c}[\rho_{He}]}{\delta \rho_{He}} \right] \Psi_{He}(R_{He})$$

(4a)

$$\frac{i\hbar}{\partial t} \phi_{X_2}(\theta, \phi) = \left[ \frac{-\hbar^2}{2\mu_{X_2} r_{eqX_2}} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + \int dR_{He} V_{He-X_2}(\theta, \phi, R_{He}) \rho(\rho_{He}) \phi_{X_2}(\theta, \phi) \right] \phi_{X_2}(\theta, \phi)$$

(4b)

These equations are analogous to those reported in the photodissociation of $\text{Cl}_2(B \rightarrow X)$ in He$\text{N}_2$, but in the present case they involve the two angular degrees of freedom instead of the $\text{X-X}$ relative distance. In addition, eqn (4a) and (4b) have been transformed following an analogous strategy to that in ref. 36 (vibrational relaxation of $\text{I}_2$), which is more efficient to account for the dynamics when only energy transfer processes are involved. Thus, the rotational wave function has been expressed in terms of the rotational eigenfunction basis set $\{\phi_{jm}(\theta, \phi)\}$ of the rotational Hamiltonian operator corresponding to the isolated molecule (i.e., without including the interaction of $X_2$ with the helium environment). These eigenfunctions are the spherical harmonics, $\{Y_{jm}(\theta, \phi)\}$, and hence we have expressed $\phi_{X_2}(\theta, \phi)$ as

$$\phi_{X_2}(\theta, \phi) = \sum_{j,m} c_{jm} Y_{jm}(\theta, \phi)$$

(5)

Eqn (4b) can now be transformed into the differential eqn (6b), which can be solved more efficiently in terms of numerical accuracy and computational time. According to this, the equations of motion that have been used are the following:

$$i\hbar \frac{\partial}{\partial t} \Psi_{He}(R_{He}) = \left[ \frac{-\hbar^2}{2m_{He}} \nabla^2 + \sum_{i,j,m} c_{jm}^* c_{jm} V_{i,j,m}(R_{He}) + \frac{\delta_{c}[\rho_{He}]}{\delta \rho_{He}} \right] \Psi_{He}(R_{He})$$

(6a)

$$i\hbar \frac{\partial}{\partial t} \phi_{jm}(t) = E_{rot,j,m} c_{jm}(t) + \sum_{j,m} c_{jm}(t) V_{i,j,m}(R_{He})$$

(6b)

$$i = 0, 1, 2, \ldots, n \ m_l = -i, \ldots, 0, \ldots, i$$

where $\{E_{rot,j,m}\}$ are the associated rotational eigenvalues of the free molecule, and the helium coordinate-dependent, $V_{i,j,m}(R_{He})$, and the ordinary, $V_{i,j,m}(j)$, potential energy matrix elements are given by

$$V_{i,j,m}(R_{He}) = \sum_{i,m} \sin \theta d\theta d\phi V_{He-X_2}(\theta, \phi, R_{He}) Y_{i,m}^*(\theta, \phi) Y_{j,m}(\theta, \phi)$$

(7a)

$$V_{i,j,m}$$

(7b)

Several static and dynamic calculations have been performed in order to select the number of functions included in the basis set. For the selected systems, it has been found that for an initial excited rotational state $(j_0,m_0 = 0)$, produced from the excitation of the $(j = 0, m_0 = 0)$ ground state, only states with even $\Delta j$ and $m_j = 0$ are needed. For a given initial excited state $(j_0,m_0 = 0)$, in order to converge the time propagation of eqn (6a) and (6b) it is enough to include in the calculations the rotational states with even $\Delta j$ and $m_j = 0$ from $(j_0,m_0 = 0)$ to $(j = j_0 + 6, m_0 = 0)$. That is, only up to three basis functions above the initial rotational exit state have been needed, as it was analogously observed in ref. 36 for the vibrational relaxation of $\text{I}_2$.

The initial time ground state of the doped nanodroplet has been obtained (static calculation) by finding the lowest energy solution of eqns (6a) and (6b). To do this, we have followed an analogous strategy to that for the time evolution (dynamic calculations; see below), but employing the imaginary time step propagation method, varying simultaneously the helium density and the molecular wave function, while keeping the number of He atoms of the nanodroplet constant (see, e.g., ref. 41). The resulting rotational wave function is constituted of the $(j,m_j)$ state $(0,0)$, with negligible contributions of the $(2,0)$, $(4,0), (6,0), \ldots$ rotational states (populations below/much below $10^{-10}$). This result probably mainly arises from both the large energy separation between the rotational states and the rather small molecule–helium interaction potential energy.

The time evolution of the helium effective wave function (eqn (6a)) has been calculated numerically by discretising the space into a grid of points and the kinetic energy terms have been determined using the fast Fourier transform (FFTW package). A fourth order predictor-corrector method, initiated by a fourth order Runge–Kutta method, has been used for the numerical propagation and the time step is equal to $1.5 \times 10^{-3}$ ps.

The Cartesian grid has a spacing of 0.40 Å for all axes and each one of them has a total length of 38.0 Å. Besides, in order to avoid artificial reflections, a quartic negative imaginary potential (NIP) has been placed at the edges of the Cartesian grid, so as to absorb the helium wave function fragments.
located outside the nanodroplet arising from evaporation of some helium atoms. The NIP is given by the following expression:

\[ V_{\text{NIP}} = -i\frac{\hbar}{4} \left( \frac{d - d_{\text{NIP}}}{L} \right)^4 \]  

(8)

The absorption strength (A) is equal to 331.0 K, the length (L) has a value of 1.0 Å, and this potential has been placed at a distance (d_{\text{NIP}}) of 1.0 Å before the limit of the grid.

For the numerical time propagation of eqn (6b) the basis set functions have been discretised, using an angular grid of 50 points between 0 and π for the angle θ and of 100 points between 0 and 2π for the angle φ. Then, to propagate in time, the following steps, which are analogous to those of ref. 36, have been followed:

1. At a given time \( t \), the matrix representation of the full effective rotational Hamiltonian of \( X_2 \) (eqn (4b)), \( H_{\text{rot}} \), which is expressed in terms of \( \{ i,m_j \} \), is diagonalized, obtaining \( H_{\text{a}} \).

2. In the new rotational basis set \( \{ | \alpha \rangle \} \) just determined the time evolution \( t \rightarrow t + \delta t \) of the coefficients \( c_\alpha \) of the \( X_2 \) rotational vector state is easy to achieve, as we are considering stationary states: \( c_\alpha (t + \delta t) = c_\alpha (t) e^{-\delta t \text{a} \cdot \text{b} \cdot \text{h}} \).

3. The \( c_{i,m_j}(t + \delta t) \) coefficients are now calculated from the \( c_\alpha (t + \delta t) \) ones coming back to the reference basis set \( \{ i,m_j \} \).

4. Steps (1)–(3) are repeated for the time evolution \( t + \delta t \rightarrow t + 2\delta t \) and so on for the following times, until the propagation is completed.

The Hamiltonian matrix has been diagonalized using the Jacobi method as it is a real and symmetric matrix. This procedure is faster and much more numerically stable than the usual method applied to solve eqn (4b)\(^{41-43} \) (here the error only comes from the diagonalization and round-off numerical computer errors). This computational strategy has been essential to make the present study possible, as the rotational relaxation processes can be particularly slow in superfluid liquid helium nanodroplets.

3. Results and discussion

The rotational energy relaxation of several isotopes of hydrogen \( (\text{D}_2, \text{T}_2, \text{Q}_\text{a}_2, \text{Q}_\text{i}_2 \text{ and S}_\text{x}_2) \) embedded in a superfluid helium nanodroplet of one hundred \(^4\text{He} \) atoms has been investigated, considering a sudden excitation of the molecule from the rotational ground state \( (j = 0, m_j = 0) \) up to a given rotational excited state (even \( j, m_j = 0 \)).

The selection of a small helium nanodroplet, \(^4\text{He}_{100} \), is based on computational reasons, as in the case of the theoretical study of the vibrational relaxation.\(^{36} \) Rotational relaxation processes imply long time scales, so a large number of propagation steps is needed to solve the equations of motion and complete the simulations. Moreover, as this relaxation process is expected to involve mainly the interaction between the molecule and the first and second helium solvation shells, the selected size of the nanodroplet seems reasonable (this will be confirmed in Section 3.3). The radial helium density of the

\[
\rho_{\text{H}}(j = 0, m_j = 0)@(4\text{He})_{100} \text{ ground state doped nanodroplet along the } x, y \text{ and } z \text{-axes.}
\]

\[ H_{\text{D}_2}(j = 0, m_j = 0)@(4\text{He})_{100} \text{ ground state doped nanodroplet is shown in Fig. 1 and is identical for all the isotopes.}
\]

3.1 Rotational relaxation of \( X_2(j = 2, m_j = 0) \) vs. rotational constant

The time evolution of the \( (j = 2, m_j = 0) \) and \( (j = 0, m_j = 0) \) state populations for the five selected molecules is shown in Fig. 2. Besides, the essentially negligible \( (j = 0, m_j = 0) \) \( \text{H}_2 \) population is also given for illustrative purposes, showing that relaxation from \( (j = 2, m_j = 0) \) is particularly slow for this isotope (only a population of the order of \( 10^{-7} \) has been obtained for the rotational ground state, after 7 ns of simulation). This fact has made us focus in this work on the \( \text{D}_2, \text{T}_2, \text{Q}_a, \text{Q}_i \text{ and S}_x \) species. From these results it comes out that the \( (j = 2, m_j = 0) \) state is metastable in these systems, because relaxation takes quite a lot of time.

The state populations can be successfully modeled using the sigmoid function. Thus, the \( (j = 0, m_j = 0) \) population vs. time has been taken as equal to \( 1 / [1 + \exp(-k(t - t_0))] \), where \( k \) and \( t_0 \) are constants that depend on the system \( [k \text{ is related to the}
\]

\[
\text{Fig. 1} \quad \text{Helium radial density of the } H_2(j = 0, m_j = 0)@(4\text{He})_{100} \text{ ground state doped nanodroplet along the } x, y \text{ and } z \text{-axes.}
\]

\[
\text{Fig. 2} \quad \text{Populations of the } (j = 0, m_j = 0) \text{(solid lines) and } (j = 2, m_j = 0) \text{(dashed lines) rotational states of the molecules, as a function of time.}
\]
The coupling between the two involved states and $t_0$ is the time for which the ($j = 0$, $m_j = 0$) population is 0.5 (Fig. S1, ESI†). This equation was recently obtained by us modeling the vibrational relaxation in HeNDs using a Hermitian non-linear two-state Hamiltonian operator.36

The values of the global relaxation times, lifetimes and transition times of the ($j = 2$, $m_j = 0$) excited state are gathered in Table 1 and plotted in Fig. 3. The global relaxation time has been taken from $t = 0$ to the time corresponding to a population of this state equal to 0.01. The lifetime is defined from $t = 0$ to the time corresponding to a population of 0.5 of the same state. The transition time is defined as the time it takes for the population of this state to decay from 0.99 to 0.01.

These three properties are of the order of nanoseconds and they increase in a significant way with the rotational constant $B_e$ (i.e., when the mass decreases), which leads to an increase of the energy gap between the rotational states (Table 1). Thus, for ($j = 2$, $m_j = 0$) the global relaxation times, lifetimes and transition times are in the 1.32–5.33 ns, 1.01–4.17 ns and 0.64–2.36 ns intervals, respectively. Moreover, if we take as a reference, e.g., the values of the Sx₂ properties, for each isotopic variant the three properties, expressed in relative terms, take quite similar values (around 1.0, 1.2, 1.7 and 3.9 for Qi₂, Qa₂, T₂, and D₂, respectively).

Fig. 3 shows the global relaxation times, lifetimes and transition times for ($j = 2$, $m_j = 0$) and the fitting curves (quadratic polynomials) by which the results have been satisfactorily described. By extrapolation according to these curves, for H₂($j = 2$, $m_j = 0$) in HeNDs these properties are estimated to be ≈26.3, ≈20.8, and ≈10.1 ns, respectively (Table 1). The interpretation of these results will be given at the end of this section, after consideration of other properties of the system.

Unfortunately, there is no previous information available on the rotational lifetimes of the molecules studied here to compare with, but there are some estimated experimental data on HF($j = 1$)² and HCl($j = 1$)⁶ in HeNDs (lifetimes ≥12 and ≥5.3 ps, respectively). Because of this, we have carried out a model calculation on the relaxation of T₂($j = 2$, $m_j = 0$) considering the H₂–He interaction potential energy multiplied by a factor equal to 3.597, in order to make it more similar to the HF–He one [$V_{min}$(HF–He)⁶¹/$V_{min}$(H₂–He)]⁶² = 3.597.⁶²,⁶³ The T₂ molecule was selected as it has a rotational constant (20.3350 cm⁻¹) that is similar to that for HF (20.9557 cm⁻¹).⁶⁰

The calculated lifetime of T₂($j = 2$, $m_j = 0$) obtained using this model (3.597 V(H₂–He)) led to a lifetime estimate of ~120 ps (while the value obtained using the real V(H₂–He) potential energy was 1785 ps). Moreover, if we had also taken into account that the anisotropy of V(HF–He) is larger than that for V(H₂–He), an even lower lifetime value would be expected for HF in a HeND. Thus, this model calculation suggests that the theoretical approach employed here is reasonable, at least as an initial step, to describe the rotational energy relaxation of molecules in HeNDs.

The experimental data on molecular rotational dynamics is also very limited in the case of ordinary liquids, although a few

Table 1 Global relaxation times, lifetimes, and transition times of the ($j = 2$, $m_j = 0$) rotational state for all molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$B_e$ (cm⁻¹)</th>
<th>Global relax. time (ps)</th>
<th>Lifetime (ps)</th>
<th>Transition time (ps)</th>
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<td>Sx₂</td>
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<td>1321</td>
<td>1008</td>
<td>636</td>
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<tr>
<td>Qi₂</td>
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<td>1371</td>
<td>1047</td>
<td>656</td>
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<tr>
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<td>1606</td>
<td>1233</td>
<td>757</td>
</tr>
<tr>
<td>T₂</td>
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<td>2311</td>
<td>1785</td>
<td>1063</td>
</tr>
<tr>
<td>D₂</td>
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<td>5329</td>
<td>4167</td>
<td>2357</td>
</tr>
<tr>
<td>H₂</td>
<td>60.8530</td>
<td>26.335</td>
<td>20.755</td>
<td>10.138</td>
</tr>
</tbody>
</table>

a The experimental values from ref. 60 have been used. b Extrapolated values from a quadratic polynomial fitting.
direct measurements have been reported in this context, with some of these studies including molecular dynamics (MD) simulations. Theoretical information has been reported on the rotational relaxation of \( \text{H}_2 \) and \( \text{D}_2 \) in supercritical liquid Ar,76,71 and in near critical liquid CO\(_2\),66 and also on the relaxation of other systems (e.g., \( \text{CN} \) in liquid Ar\(^7\)). In the former case (Ar(0) at 299.5 K) the lifetime of the \( j = 2 \) state in the relaxation to \( j = 0 \) is about 3.6 and 2.0 ps for \( \text{H}_2 \) and \( \text{D}_2 \), respectively (perturbation theory results evaluated by MD simulations). In the second case (CO\(_2\)(0) at 308 K) a substantially larger lifetime (somewhat above 34 ps) can be estimated from the MD simulation results for \( \text{D}_2 \). This last result is about 17 times larger than when \( \text{D}_2 \) is in supercritical liquid Ar, which probably arises from the diverse nature of the solvents (the \( \text{D}_2-\text{Ar} \) and \( \text{D}_2-\text{CO}_2 \) interactions have different strength and anisotropy; see also ref. 73 and 74 (\( V_{\text{min}} = -56.5 \) and \(-211.932 \text{ cm}^{-1} \), respectively) and their different number densities (40.0 M vs. 8.5 M for Ar(0) and CO\(_2\)(0), respectively; in both cases very far from an infinite dilution solution).

These situations are, of course, very different from the \( \text{D}_2 \) molecule embedded in a He\(_{\text{ND}}\), where the interaction of the molecule with the solvent is much weaker than in the case of the ordinary liquids, which, in addition, are at much higher temperature (additionally, the \( \text{D}_2 \) molecule in the nanodroplet cannot interact with other species of the same type). Hence, it is reasonable to obtain much larger rotational lifetimes using as a solvent superfluid helium than when using ordinary liquids, as we have obtained here.

Regarding the molecular state after relaxation, it is essentially identical to \( \{ j = 0, m_j = 0 \} \), as the populations of the other states are clearly below \( 10^{-6} \). This means that the helium environment does not significantly affect the rotational structure of the \( \text{X}_2 \) molecule, as we have already observed in the calculation of the ground state of the doped nanodroplet. This is probably due to the important rotational energy differences and the weak \( \text{H}_2^{(4}\text{He})_{100}\) vdW interaction potential energy (\( \approx -100 \text{ K} \)).

The expected value of \( \cos^2\theta \) vs. time varies with the composition of the wave function, as it is shown in Fig. 4. At the initial times of the simulations \( \langle \cos^2\theta \rangle \) remains essentially constant (0.522) and oscillates with a significant amplitude during the transition (between \( \approx 0.10 \) and \( \approx 0.75 \)). Once the transition to the \( \{ j = 0, m_j = 0 \} \) state has been completed, \( \langle \cos^2\theta \rangle \) finally reaches a value of 0.333. Moreover, the expected value of \( \cos^2\phi \) is constant and equal to \( \frac{1}{2} \) for all rotational states, and the expected value of the \( J^2 \) operator vs. time varies in a smooth way from \( 6\hbar^2 \) to \( 0\hbar^2 \), values that correspond to the \( \{ j = 2, m_j = 0 \} \) and \( \{ j = 0, m_j = 0 \} \) states, respectively (Fig. S2, ESI†).

The total energy of the system \( \{ \text{X}_2@\text{HeND} \} \) decreases when relaxation is taking place, and this decrease is larger when the \( B_e \) value increases (i.e., for the lighter isotopes), finally obtaining the same total energy for all the molecules (Fig. 5). This means that the bigger the rotational constant \( B_e \), the more energy a single evaporated \( ^4\text{He} \) atom carries with it (the important amount of energy released by the atom will be analysed in more detail later). Unlike the other cases, for the \( \text{H}_2 \) molecule the excited doped nanodroplet has positive energy, due to the large value of the \( j = 2 - j = 0 \) energy separation.

The relaxation of the liquid helium (which takes place thanks to the evaporation of some He atoms) needs a time that is basically coincident with that of the rotational relaxation. Thus, comparison of the \( \{ \text{X}_2@\text{HeND} \} \) energy at the global relaxation time with the corresponding ground state (i.e., fully relaxed) value reveals differences of 0.03, 0.01, 0.08, 0.19 and 0.45% for \( \text{Sx}_2, \text{Qx}_2, \text{Qa}_2, \text{T}_2 \) and \( \text{D}_2 \), respectively. Since the main

![Fig. 4](image1.png)  
**Fig. 4** Expected value of \( \cos^2\theta \) for the \( \{ j = 0, m_j = 0 \} \) -- \( \{ j = 2, m_j = 0 \} \) relaxation of the molecules vs. time.

![Fig. 5](image2.png)  
**Fig. 5** \( \{ \text{X}_2@\text{HeND} \} \) total energy (top) and number of \( ^4\text{He} \) atoms of the He\(_{\text{ND}}\) (bottom) for the \( \{ j = 2, m_j = 0 \} \) rotational relaxation of the molecules vs. time.
priority of this study has been to investigate the rotational relaxation and also for computational reasons, we have stopped the calculations some time after verifying that the rotational relaxation has been completed.

Rotational relaxation mainly arises from the interaction of the molecule with the He atoms of the first and second solvation layers (cf. Section 3.3) and other properties of interest during the molecular relaxation are as follows: (a) the rotational energies of the molecules evolve in an analogous way and according to the \((j = 2, m_j = 0)\) relaxation; \(\Delta E_{\text{rot}}\) energy gap \((8.55–262.81 \text{ K range from Sx}_2\) to D\(_2\), respectively\), following the evolution of the populations\({(\text{b})}\) the energy of helium in the nanodroplet increases by \(\approx 4.7 \text{ K}\) [this value is similar to the increase of the helium energy observed in the vibrational relaxation of \(\text{I}_2\) in \(\text{HeNDs}\)] \((\approx 4.4 \text{ K for each} 4\text{He atom evaporation}; \Delta E_{\text{vib}} = 308.621 \text{ K, i.e., of the same order of magnitude as the present rotational energy differences}]\); (c) the \(\text{X}_2–\text{HeND} \) interaction potential energy depends very little on the molecule, as it is essentially constant (a global change of \(\Delta E_{\text{int}} \approx -0.07 \text{ K}\)); and (d) the structure of the nanodroplet does not change appreciably.

The nanodroplet structure has been characterized in terms of the helium density, which remains practically constant and preserves the initial spherical symmetry (cf. Fig. S3 and S4, ESI† where the \(T_2 \) relaxation is presented as an illustrative example). Since for all the excited rotational states \(m_j\) is equal to zero, there is a higher probability of finding the molecular axis located in the vicinity of the \(z\) axis. Then, one would expect a certain ellipsoidal deformation of the nanodroplet before the relaxation to the ground rotational state, but this is not the case as indicated above. This is probably a consequence of the superfluid helium nature and the weakness of the molecule–helium interaction.

It should be noted that in all cases, as a result of the model used to describe the superfluid helium (continuous character of the density functional approach), a very small amount of helium is evaporated before the molecular relaxation takes place (Fig. 5). This arises from very small changes suffered by the liquid due to the initial sudden excitation of the molecule. As an example, in the case of the excited \(\text{H}_2\), during the 7000 ps time interval investigated, a total of 0.13 He atoms are evaporated.

Furthermore, from the calculations it comes out that superfluid liquid helium efficiently releases its excess energy resulting from the rotational relaxation process, as is expected for a superfluid. However, the number of evaporated He atoms (a single atom in all cases) is smaller than the ratio between the energy to be released \(\Delta E_{\text{rot}}\) and the binding energy of a He atom in the nanodroplet \(7.2 \text{ K}\). Thus, ratio values of 12.2, 14.6, 18.2, 24.4, and 36.5 have been obtained for \(\text{Sx}_2\), \(\text{QI}_2\), \(\text{QA}_2\), \(\text{T}_2\) and \(\text{D}_2\), respectively, taking into account that, according to the experiments\(73\) the evaporated atoms carry a negligible amount of translational kinetic energy (as it is close to the thermal value at \(T = 0.37 \text{ K}\)). The excitation energy essentially serves to break the vDW bonds between the He atoms that will be evaporated and the nanodroplet, and this will lead to the stabilization of the system.

This discrepancy has already been reported for other physico-chemical problems, such as, e.g., the vibrational energy relaxation of \(\text{I}_2\) (ref. 36) and the formation of \(\text{Ne}_2\) (ref. 46) inside a HeND, employing an analogous theoretical approach. This probably results from the continuous character of the DFT method used to account for the superfluid liquid helium, as it can allow liquid helium to depart from the nanodroplet with excess energy. Then, the transformation of the amount of liquid helium evaporated into discrete He atoms would yield a smaller number of evaporated atoms.

In spite of this difference, it should be highlighted that in the present study the interaction between the molecule and the liquid helium has been described using the best \(\text{H}_2–\text{He} \) intermolecular potential energy available, the superfluid character of helium has been taken into account employing the best density functional available and, as we will see in Section 3.3, the two first helium solvation shells are clearly the main ones involved in the relaxation process. Based on these facts and the comparisons previously reported, we believe that the results obtained here are reasonable.

To interpret the relaxation time results, the coupling term between the \((j = 2, m_j = 0)\) and \((j = 0, m_j = 0)\) states (cf. eqn (7)) has been analyzed, since it is expected to influence the transition probability in an important way (more exactly, we have examined the coupling squared terms, \(V_{ij}\), where \(V_{ij}\) take real values). The initial, average, maximum and minimum \(V_{ij}\) values for the transition time interval are shown in Table S1 (ESI†). For all isotopes coincident values have been obtained for the initial \(V_{ij} (1.4 \times 10^{-3} \text{ K}^2)\) and similar results have been found for the average \(V_{ij} (3.2 \times 10^{-4}–3.5 \times 10^{-3} \text{ K}^2)\). The maximum values are less similar \((1.0 \times 10^{-5}–1.6 \times 10^{-2} \text{ K})\) and the minimum ones in general differ \((2.4 \times 10^{-8}–4.7 \times 10^{-4} \text{ K}^2)\) and are lower or substantially lower than the other \(V_{ij}\) values.

Given the similarity of the initial and average couplings, it does not seem feasible to interpret the results based on the coupling terms. It is reasonable to think that the different relaxation times are probably due to a property that is different enough for the five isotopic species, i.e., the velocity at which they move. From the angular velocity \(\omega\) associated with a given rotational state, the corresponding linear velocity \(v\) can be found, and it comes out that the \(v\) values are at least one order of magnitude greater than the velocity of the He atoms of the nanodroplet \((\nu = 699, 839, 1049, 1402\) and \(2099 \text{ m s}^{-1}\) for \(\text{Sx}_2\), \(\text{QI}_2\), \(\text{QA}_2\), \(\text{T}_2\) and \(\text{D}_2\), respectively, while \(\nu_{\text{He}} = 50 \text{ ms}^{-1}\)). The progressively more difficult relaxation observed from \(\text{Sx}_2\) to \(\text{D}_2\) correlates with the fact that the molecular velocity is increasingly higher than that of the He atoms.

The dependence of the molecular relaxation times on the rotational constant \((a_0 + a_1 B_a + a_2 B_a^2)\) (Fig. 3) has its origin in the quadratic polynomial dependence of these time properties on the angular velocity \(\omega = 4\pi B_0 \left(\frac{j(j+1)}{2}\right)^{1/2}\) for a rigid rotator; \(B_0\) in frequency units). Some additional plots to show in a more clear way the behaviors found are presented in Fig. S5 (ESI†), where the inverse of the relaxation time properties vs. \(1/B_0\) and these inverse values relative to those of \(\text{Sx}_2\) vs. \(B_0\) are given. Quadratic (with the linear term being the most important one)
and linear dependences are found, respectively. The complexity of these systems, due to the presence of a superfluid quantum liquid, makes it very difficult to go beyond qualitative considerations.

In this context it is helpful to represent in a single plot the temporal evolution of the different components of the helium energy, according to the OT functional, the $E_{\text{X}_2}$–helium interaction energy and the $V_0$ term, so as to have a somewhat more complete perspective of the dynamics (Fig. S6, ESI†). The $T_2(j = 2, m_j = 0)$ relaxation has been shown as a representative example, and it is worth noting that, during the transition time, the $T_2$–helium interaction energy and the $(j = 2, m_j = 0)$–$(j = 0, m_j = 0)$ $V_0$ coupling term show oscillations of significant amplitude. Besides, the kinetic energy of helium initially increases a little bit, reaches a maximum and then decreases slightly below its initial value. Then, the transition approximately begins when the helium is finally able to accept a very small amount of kinetic energy from the molecule (the helium kinetic energy seems to play the role of “switch” of the relaxation process).

3.2 Rotational relaxation of $S_{X_2}(j, m_j = 0)$ vs. $j$

The rotational relaxation of an $S_{X_2}$ molecule embedded in a superfluid helium nanodroplet of 100 $^4$He atoms, considering a sudden excitation from the rotational ground state ($j = 0, m_j = 0$) to three different excited states ($j, m_j$), (2, 0), (4, 0) and (6, 0), is analyzed in this section.

The temporal evolution of the rotational states populations for the three relaxations of $S_{X_2}$ investigated is shown in Fig. 6. The global relaxation times for $(j_0 = 2, m_{j_0} = 0)$, $(j_0 = 4, m_{j_0} = 0)$ and $(j_0 = 6, m_{j_0} = 0)$ are equal to 1.32, 4.27 and 12.30 ns, respectively. Therefore, rotational relaxation becomes more difficult as rotational excitation increases, in sharp contrast to what happens for vibrational relaxation. Vibrational relaxation is faster for higher vibrational energies as in this case the molecule vibrates with larger amplitudes, interacting in a stronger way with the neighbouring liquid helium, and due to this it is easier for helium to oscillate in phase with the diatomies. See Section 3.4 for more details.

The lifetime of the initial rotational states, 1.00, 2.80 and 7.58 ns for (2,0), (4,0) and (6,0), respectively, increases in an important way with the energy gap with respect to the immediately lower allowed state, which increases with $j$ (Fig. 7): $\Delta E_{\text{Rot,2} \to 0} = 87.55$ K, $\Delta E_{\text{Rot,4} \to 2} = 204.29$ K, and $\Delta E_{\text{Rot,6} \to 4} = 321.03$ K. Besides, transitions to lower rotational states are faster when $j$ decreases. The lifetime of each rotational state and the duration of the transitions are given in Tables 2 and 3, respectively. The increase of the lifetime with increasing $j$ has also been reported in theoretical calculations on $H_2$ and $D_2$ in ordinary liquids. The interpretation of the relaxation time properties will be presented at the end of this section.

From Fig. 6 it can also be seen that rotational relaxation takes place approximately according to a cascade mechanism: the de-excitation process involves several sequential steps $(j_0 \to j_0 - 2; j_0 - 2 \to j_0 - 4; \ldots; 2 \to 0)$. Besides, for a given $j$ state, the $j - 4$ state starts being populated before the $j - 2$ state is completely populated and the $j$ state is completely unpopulated, which implies that there is no metastability for the intermediate rotational states.

The expected values of $\langle \cos^2 \theta \rangle$ for the initial rotational levels $j_0 = 2, 4,$ and 6 are equal to 0.522, 0.503 and 0.499, respectively, and they decrease to a value of 0.333 (Fig. 8). Oscillations in $\langle \cos^2 \theta \rangle$ are particularly intense when the transitions are taking place. In addition, $(j^2)$ evolves in a smooth manner from 6, 20 and 42 $h^2$, corresponding to $j_0 = 2$, 4, and 6, respectively, to $0h^2$, with intermediate quasi-steps for each de-excitation (at $\approx 6h^2$ for $j_0 = 4$ and at $\approx 20h^2$ and $\approx 6h^2$ for $j_0 = 6$; cf. Fig. S7, ESI†).

In the molecular relaxation process the energy of the doped nanodroplet decreases progressively, presenting quasi-steps that correspond to the intermediate rotational states involved, Fig. 6 Populations of the $S_{X_2}(j, m_j = 0)$ states for three different initial excitations, $(j_0, m_{j_0} = 0)$, as a function of time: (2, 0), (4, 0) and (6, 0), from the top to the bottom, respectively.
and a single helium atom is evaporated in each \( j \to j - 2 \) transition (Fig. 9). Comparison of the Sx2@HeND energy at the global relaxation time with the ground state value shows differences of about 0.03, 0.22 and 0.83% for the initial excitations to \( (j, m_j = 0) \), \( (j = 4, m_j = 0) \) and \( (j = 6, m_j = 0) \), respectively. Besides, analogous comments to those given in Section 3.2 on the rotational energy of the molecules, energy of helium in the nanodroplet, \( X_2 - \text{HeND} \) interaction potential energy and structure of the nanodroplet apply here.

Concerning the relaxation times, since in this case for each \( j \to j - 2 \) transition there are different coupling term (Table S1, ESI†) and angular velocity values, even for the sequence of relaxations for which there is more information available \( (j_0 = 6 \to j = 4; j = 4 \to j = 2; j = 2 \to j = 0) \) it is not possible to characterize the type of dependence that the lifetime and transition time have on \( V_{ij} \) and \( \omega \). Besides, regarding the \( j \to j - 2 \) couplings it is worth mentioning that the associated \( V_{ij} \) average term increases in a substantial manner with the degree of excitation (Table S1, ESI†), and shows an almost linear dependence on \( j(j + 1) \), i.e., on the rotational energy, as \( B_e \) is constant here. Thus, for instance if we pay attention to the \( V_{ij}^2 \) average value for the sequence of relaxations \( j_0 = 6 \to j = 4, j = 4 \to j = 2 \) and \( j = 2 \to j = 0 \) and take as a reference the value of \( j = 2 \to j = 0 \), the following average values are obtained: 34.2, 11.2 and 1.0, respectively.

As the coupling strongly favors the relaxations involving higher \( j \) levels and we observe that the relaxation times are

---

### Table 2

<table>
<thead>
<tr>
<th>( j )</th>
<th>2</th>
<th>4</th>
<th>6</th>
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<tr>
<td>Lifetime (in ps) of each Sx2 rotational state for three initial excitations</td>
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### Table 3

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<th>6  ( \to ) 4</th>
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</tbody>
</table>

\( a \) \text{Max}((|j = 2, m_j = 0| |\phi(t)|)^2) = 0.9680. \text{Max}((|j = 4, m_j = 0| |\phi(t)|)^2) = 0.9669. \text{Max}((|j = 6, m_j = 0| |\phi(t)|)^2) = 0.9686.
larger for these levels, we can conclude that the angular velocity of the molecule is playing a dominant role, leading to more difficult relaxation when higher $j$ levels are considered. With respect to the temporal evolution of the different components of the helium energy, $S_{xj}$–helium interaction energy and $V_{ij}$, analogous results to those reported in the previous section apply in the present situation.

3.3 Rotational relaxation of $T_2(j = 2, m_j = 0)$ vs. nanodroplet size

The rotational relaxation of $T_2(j = 2, m_j = 0)$ inside a superfluid helium nanodroplet has been studied considering several nanodroplet sizes ($N = 25, 50, 75, 100$ and 125), in order to investigate the effect of the size on the relaxation process.

The helium radial density of the ground state doped nanodroplets $T_2(j = 0, m_j = 0)@^{4}\text{He}_{N}$ along the three axes is plotted in Fig. 10, where the evolution of the first and second solvation shells with $N$ can be seen. The number of He atoms in the first solvation layer is moderately modified with $N$ ($N_{\text{solv,1}} = 14.6, 14.5, 14.2, 13.6$ and $12.0$ for $N = 125, 100, 75, 50$ and 25, respectively). However, significant changes are evident in the second solvation layer, whose size is reduced in an important way when the number of He atoms of the nanodroplet decreases. As the interaction between the molecule and the liquid helium probably mainly involves the first solvation layer with some contribution of the second one, the effect of the nanodroplet size on the rotational relaxation is expected to be noticeable, with similar results for the two nanodroplets of larger size.

The time evolution of the $(j = 2, m_j = 0)$ and $(j = 0, m_j = 0)$ populations for the five nanodroplet sizes is presented in Fig. 11, where it can be seen that the results obtained for the nanodroplets with $N = 100$ and $N = 125$ are quite similar (see also Table 4). The global relaxation times, lifetimes and transition times are in the $2.28–2.93$ ns, $1.76–2.27$ ns and $1.05–1.32$ ns, respectively. However, significant changes are evident in the nanodroplet size results from the increase of the interaction between the molecule and the liquid helium of the HeND as $N$ increases. For bigger nanodroplets the helium environment surrounding the impurity is denser and the interaction becomes stronger (the interaction energy varies from $E_{\text{int}}(N = 25) = -81.248$ K to $E_{\text{int}}(N = 125) = -105.160$ K).

This coupling increase happens when increasing the size of the nanodroplet as the helium occupation of the main solvation layers (i.e., the first and second layers) increases. Once these layers are completed, increasing the nanodroplet size does not change in a substantial way the molecule–helium interaction energy, so the time scales of the rotational relaxation are stable and correspond to defined saturation values of the global relaxation times, lifetimes and transition times.

Furthermore, it is possible to analyze the dependence of the temporal properties on the coupling ($V_g$ average), which depends on the nanodroplet size (Table S1, ESI†). The inverse of the relaxation time properties shows a linear dependence on the coupling between the two rotational states involved (Fig. S8, ESI†). Also, as the coupling depends linearly on the $T_2$–helium interaction energy, this implies that the inverse of the
relaxation time properties also depends in a linear way on the interaction energy (which presents a smooth but not linear dependence on N).

The set of results obtained for all the initial conditions analyzed in this work suggests that, in the rotational relaxation of diatomic molecules in superfluid helium nanodroplets, the transition time frequency increases linearly with the coupling ($V_{ij}^2$ average), while its dependence on the angular velocity, whose increase makes the transition more difficult, is more complex (quadratic dependence on $1/\nu_\alpha$, although the most important term of the corresponding polynomial function is linear). The same trends are also evident for the other relaxation time properties.

For a transition between two specific states, the use of the Fermi golden rule (first order perturbation theory context), which is often employed in spectroscopy and scattering, leads to a dependence of the transition time frequency that would simply be proportional to the associated $V_{ij}^2$ term. More complex situations could lead, e.g., to a dependence proportional to $V_{ij}^2$ and inversely proportional to $R_{NN}$, which is not the present case.

### 3.4 Rotational relaxation vs. vibrational relaxation

To achieve a better understanding of the rotational energy relaxation dynamics inside HeNDs, it is useful to compare the results obtained here with recently reported vibrational energy relaxation data ($I_2$ in HeNDs and analogous theoretical approach). VER also occurs following sequential transitions, above $N=100$ there is also a small influence of $N$ on the lifetime, and heavier isotopes could lead, e.g., to a dependence proportional to $V_{ij}^2$ and inversely proportional to $R_{NN}$, which is not the present case.

However, in contrast to the RER results, for VER when the initial excitation increases a decrease is observed in the lifetime of the excited vibrational state. This difference can be interpreted in a rather simple way taking into account that RER and VER are associated with very dissimilar types of motion/degrees of freedom. Thus, when vibrational excitation increases: (a) the motion frequency is approximately constant and equal to $\nu_\alpha$ (for low-moderate excitations); (b) the energy separation $\nu \leftrightarrow \nu-1$ is approximately constant ($\hbar\nu_\alpha$); and (c) the interaction with helium is stronger as the vibrational amplitude increases.

It should also be noted that in the case of VER metastability has been observed for intermediate excited states, in contrast to what happens for RER.

The results obtained in this work on rotational relaxation seem reasonable and the numerical methods employed to solve the Schrödinger-like equations for long time simulations are efficient. We expect that this initial theoretical study will be useful to motivate further analysis on this interesting and not easy to investigate relaxation process.

### 4. Summary and conclusions

The rotational energy relaxation of a homonuclear diatomic molecule inside a superfluid helium nanodroplet has been investigated using a hybrid theoretical approach analogous to that proposed recently by us for the study of vibrational energy relaxation in a HeND. The helium and molecule dynamics have been described using a hybrid approach (TDDFT and standard quantum dynamics methods, respectively). To the best of our knowledge this is the first theoretical study about rotational relaxation of molecules inside liquid helium nanodroplets.

Several real ($D_2$ and $T_2$) and hypothetical ($Qa_2$, $Qi_2$ and $Sx_2$) isotopes of $H_2$ have been examined in order to make the investigation easier (taking advantage of the large rotational constants of the selected systems) and allowing us to explore the influence of the rotational constant $R_N$ of these fast rotors on the relaxation dynamics. The rotational relaxation from the ($j=2$, $m_j=0$) state has been considered in all cases and additional simulations have been carried out for $Sx_2$ and $T_2$, so as to determine the influence of the initial excited rotational state and nanodroplet size on the relaxation dynamics, respectively.

The structure of the HeND essentially does not change during the RER process and the superfluid liquid helium efficiently removes from the nanodroplet the energy released by the molecule during the relaxation (although the number of evaporated helium atoms is small compared with the expected values). Besides, the RER approximately occurs following sequential transitions between two “consecutive” rotational levels (cascade mechanism): $j \rightarrow j-2; j-2 \rightarrow j-4; \ldots 4 \rightarrow 2; 2 \rightarrow 0 (m_j=0)$ in this case, due to the nuclear symmetry. In addition, the $(j=0, m_j=0) \rightarrow (j=2, m_j=0)$ global relaxation time is of the order of nanoseconds (from 1.3 to 5.3 ns for $Sx_2$ and $D_2$, respectively).

Regarding the lifetime of an excited rotational state, it increases when: (a) the rotational constant increases; (b) the quantum number $j$ increases; and (c) the nanodroplet size decreases (above $N=100$ there is a small influence of $N$ on the lifetime). The study suggests that the transition time frequency increases linearly with the coupling, while its dependence with respect to the angular velocity (which makes the transition more difficult as it increases) is not so simple. A similar behavior is also found for the other time properties.

Furthermore, it has been interesting to compare rotational and vibrational relaxations. Even though both relaxation processes take place following sequential transitions, the lifetime of the excited vibrational states decreases as the excitation increases, differing from what happens for the rotational case. This discrepancy has been interpreted on the basis of the very different types of motion involved. Moreover, it is worth noting that metastability was found for intermediate excited vibrational states, unlike what happens for RER.

In future investigations it would be interesting to include the zero-point motion of the centre of mass of the molecule, which nowadays is very difficult to consider due to the very large computational resources needed. Another interesting question for future work would be to analyze the influence of the vibration-rotation coupling on the relaxation dynamics and...
to try to include the quantum correlation. We hope that this initial contribution will encourage more researchers to study this interesting issue about which our knowledge is still very limited.

Conflicts of interest

There are no conflicts of interest to declare.

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References


62 Taking into account the \(V_{\text{min}}(\text{HF–He})\) value from a more recent work (see the next reference) it comes out that the \(V_{\text{min}}(\text{HF–He})/V_{\text{min}}(\text{H}_2–\text{He})\) ratio is a bit larger (3.975).


77 Miquel Blancafort-Jorquera (University of Barcelona), Personal communication.