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The Hund paradox and stabilization of molecular chiral states

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Abstract. The "paradox of optical isomers" revealed by Hund in 1927 is re-examined taking into account the interaction of a chiral molecule with phonons of optically inactive solids below the Debye temperature θ_D. It has been shown, that in the strong coupling limit, where the dephasing rate is much higher than the energy splitting frequency, the interaction can lead to a complete loss of coherence between mirror-antipodal states of the molecule due to the phonon-induced dephasing. This, in turn, suppresses tunnelling oscillations between them, so that transitions, which are reversible in time for an isolated chiral molecule become irreversible for the same molecule placed in a low-temperature matrix. In order to propose a particular mechanism of such stabilization, contributions of a single- and multi-phonon processes in the dephasing rate have been evaluated. It has been established that only the two-phonon scattering provides the sufficiently strong dephasing in low-temperature solids. Such a two-phonon mechanism is responsible for the stabilization of molecular chiral states as long as the temperature of the medium is lower θ_D, but exceeds a few Kelvin degrees. These findings are discussed in the context of the evolutionary concept known as "the cold prehistory of life".

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1 Introduction

Certain objects of the molecular world known as "chiral" possess a structure that does not have the center of inversion or the inversion plane. Typical examples are compounds with "propeller-shaped" structure (like substituted biphenyl) or molecules (like amino acids, sugars, etc.) with the central carbon atom bound to four different substituents. Each of them can exist in the form of two mirror antipodes (enantiomers) which are spatially non-superimposable on each other, just as the left hand and the right hand. Such antipodes are usually called *laevo* and *dextro* isomers and hereinafter are denoted by the letters L (from *laevo*, "left") and D (from *dextro*, "right") following notations used in the biophysical literature.

Since the beginning of the era of quantum mechanics, a chiral molecule isolated from its surroundings and from external fields has been treated as a particle in a one-dimensional symmetric double-well potential with the only stationary energy level in each individual well (see Fig. 1). The analysis of this simplest double-well system (DWS) leads to the paradox revealed by Hund in 1927 [1]. Consider L and D isomers of a chiral molecule. Let us assume that the x coordinate on Fig. 1 represents the position of certain atom, the rotation angle of an atomic group around a bond or some other configurational coordinate of the molecule. Then the mirror-antipodal states $|L\rangle$ and $|D\rangle$ are related to wave functions localized in the left or in the right potential well, respectively. These states have a chirality but do not have a definite parity and are degenerate in energy from the quantum-mechanical standpoint. Nevertheless, they cannot be the eigenstates of the isolated molecule since for a finite barrier their wave functions overlap. Such overlapping is responsible for the lost of a definite chirality and makes the molecular eigenstates be symmetric and asymmetric combinations of the L- and D-states:

$$\begin{aligned} |+\rangle &= \frac{1}{\sqrt{2}}(|L\rangle + |D\rangle), \\ |-\rangle &= \frac{1}{\sqrt{2}}(|L\rangle - |D\rangle). \end{aligned} \tag{1}$$

As a result, we arrive at the situation where an isolated chiral molecule occurring in nature as two mirror

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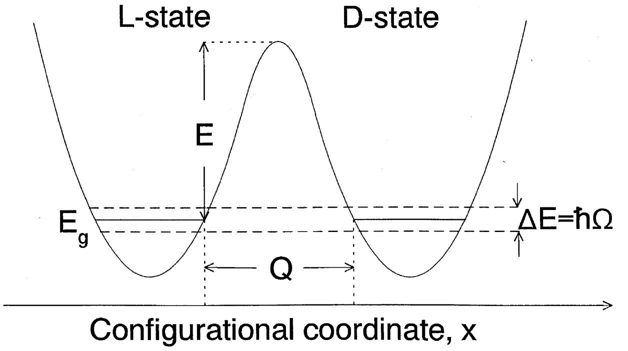

Fig. 1. Isolated chiral molecule modelled by a one-dimensional symmetric double-well system. The *L*- and *D*-states correspond to the *L*- and *D*-enantiomers of a chiral molecule, respectively. They have the same energies E_g splitted due to the quantum mechanical tunnelling. The splitting energy, ΔE, is the product of the Planck constant $\hbar$ and the tunnelling frequency Ω. Other notations: x is the configurational coordinate of a chiral molecule, E is the height of the potential energy barrier separating the *L*- and *D*-states, Q is the width of the barrier

antipodes has the states with a definite parity, rather than with a definite chirality (the Hund paradox). This, in turn, implies that the molecule will spend equal times in the *L*- and *D*-states and will tunnel back and forth between them with a characteristic frequency Ω. The latter quantity can be expressed in terms of the height of the barrier E, its width Q, the effective mass of the tunnelling particle M and the preexponential factor ν_0 as

$$\Omega = \nu_0 \exp[-(2ME)^{1/2} Q/\hbar] . \tag{2}$$

Obviously, the slower the tunnelling, the longer the lifetime of an isolated chiral molecule in the initial isomeric form. Therefore, the apparent stability of mirror antipodes relative to the spontaneous $L \rightleftarrows D$ conversion might be explained by extremely low frequencies of tunnelling oscillations. However, estimations [2, 3] carried out for real chiral molecules like amines [4] show that actually the Ω values predicted by (2) appear to be of the order of $10^7\ \mathrm{s}^{-1}$ and are too high for accepting this explanation.

Several attempts have been made to improve the situation by taking into account the weak interactions [5], collision processes [2, 6, 7], and the coupling of DWS to phonons [8–12] or photons [13] at temperature, T, low enough for neglecting the thermal activated *LD*-transitions. The potentiality of resolving the discrepancy by nonlinear wave mechanics [14] has also been discussed in the literature [3].

It has been demonstrated [2, 6–11] that the interaction of enantiomers with their low-temperature surroundings can stabilize the chiral states over the time scale longer than a period of free tunnelling oscillations $\tau_T = \Omega^{-1}$. Such an effect has been explained [5, 9] by the competition between tunnelling and various dephasing processes (e.g. collisions, coupling with the phonon bath, etc.). Such processes lead to a loss of coherence in a time τ_{dp} (the so-called dephasing time) and therefore favor the localization in the initally occupied well of an individual DWS. As a result, the medium affects dynamics of transitions in a single DWS making tunnelling oscillations damped rather than free with the damping rate dependent on a specific mechanism of dephasing [9].

The dephasing induced by the DWS-phonon coupling is of particular interest for two reasons. First, it provides a useful model for studying the role of dissipation in the tunnelling mechanisms of transport and chemical reactivity in condensed media (for review see e.g. [15, 16]. Second, the mentioned dephasing mode is quite competitive with coherent tunnelling oscillations between chiral states at low temperatures and in solid phase, i.e. under physical conditions typical for outer space. The latter circumstance enables one to expect that the phonon-induced dephasing may play an important role in the extra-terrestrial scenario of the origin of life (for review see [17–19]).

In order to clarify this point, we now turn to the most recent version of such a scenario called "the cold prehistory of life" [17, 18]. It relies on the phenomenon of the low-temperature quantum limit of a chemical reaction rate [20] and on the discovery of some fairly complex organic compound (ranging up to amino acids) in the interstellar medium [21–24]. According to this concept, the main stage of the formation of prebiotic polymers is hypothetically represented by the grains of dust of dense interstellar clouds and more explicitly, by the dirty ice mantles surrounding the cores of these grains. As any other hypothesis concerning the origin of life, the scenario under discussion should explain the typical feature of living species, i.e. the chiral purity of amino acids in all proteins (only *L*-enantiomers) and of sugars in RNA and DNA (only *D*-enantiomers). Detailed analysis of this key property of living matter [17, 18, 25] leads to the conclusion that chiral purity was achieved by spontaneous breaking of mirror symmetry in racemic organic medium containing equal numbers of *L* and *D* isomers. Various kinetic models of the mirror symmetry breaking have been the subject of active research in recent decades (see e.g. [26–34]). All of them implicitly suggest that enantiomers are able to preserve the certain "sign" of chirality during the characteristic times, τ_{ch}, of chemical processes included in a specific kinetic scheme. Such an assumption is true in "warm" scenarios since the chemical reactions go quite rapidly on the evolutionary time scale. By contrast, in the "cold" scenario, however, reaction rates can be so slow that τ_{ch} becomes comparable with τ_T. As a consequence, the *LD* delocalization in a "cold" scenario may lead to the situation where the concept of the certain sign of chirality "gets lost" over the time scales of the physical and chemical processes. However the effect of solid medium on the dynamics of tunnelling transitions in DWS [8–12] causes us to anticipate that the phonon-induced dephasing offers the way to guard against this possibility.

In the present paper we propose a mechanism of stabilization of molecular chiral states based on the detailed analysis of the phonon-induced dephasing at T below the Debye temperature θ_D. Theoretically this mechanism follows from the model for the coupling of DWS with phonons considered in the next section with special emphasis on two aspects of the problem. One aspect is the influence of dephasing on the tunnelling dynamics of

DWS, while the other concerns the evaluation of kinetic parameters describing the time evolution of the well populations. Using the density matrix formalism, we demonstrate that in the strong coupling limit the dephasing completely suppresses coherent tunnelling oscillations and that the transition between wells becomes irreversible. This corresponds to the stabilization of molecular chiral states by the solid phase environment. It is also shown that the dephasing resulting from a single-phonon process does not allow achieving the above limit and only can slightly reduce the coherence. As a consequence, the damping oscillations between wells would be expected in agreement with earlier theoretical findings [9]. Taking into account that a single-phonon dephasing appears to be inefficient, the contribution of multi-phonon processes in the Γ values is evaluated in Sect. 3. Analytical expressions for this contribution are derived for two important cases where the thermal wavelength of phonons, λ_{th}, is either longer or shorter than a typical dimension, R_s, of a molecular scattering center. The results obtained are summarized and discussed in Sect. 4. Numerical estimations made in this section indicates that the two-phonon scattering controls the dephasing rate if T exceeds *ca.* 1 K. Moreover, such a process yields the Γ values which correspond to the strong coupling limit as long as temperature is less than θ_D, but higher than a few Kelvin degrees. Our analysis enables us to conclude that the two-phonon process offers the mechanism for the stabilization of molecular chiral states under conditions typical for outer space.

2 Model for DWS coupled with phonons

Let a single chiral molecule modeled by DWS be coupled to a phonon gas of an optically inert solid. Such a coupling gives rise to the dephasing which is supposed to proceed with the rate $\Gamma = 1/\tau_{dp}$. Besides, in the case of the disordered matrix the interactions of two mirror antipodes with the same atom occupied the irregular position in the lattice cell may be distinct. For some particular orientations of a single chiral molecule with respect to the disorder surroundings, the latter circumstance can give rise to the asymmetry, E_0, of energy levels corresponding to the L- and D-states. A pictorial example is shown in Fig. 2. The evaluation of the E_0 values for such special situations represents a separate problem which is beyond the scope of the present work. Nevertheless, we will take the above asymmetry into account for generality considering E_0 as the parameter.

Our main concern in the context of the stabilization of molecular chiral states is to describe the time evolution of the probability that one of two states, say $|L\rangle$, will be populated at time $t > 0$ if initially it has been the only occupied state of an individual DWS. To achieve this objective, we first analyze the time behavior of the well populations in terms of the density matrix supposing that the main physical parameters characterizing DWS are known. In addition to E_0 and Γ, they include the coherent tunnelling frequency Ω and the rate of the incoherent tunnelling transitions W. Since the effect of dephasing on the transition probability is of primary interest here, our consideration is restricted to the case, where T is less than θ_D, but exceeds both $\hbar\Omega/k_B$ and E_0/k_B. As shown in the first part of this section, the decay of the population in the limit of strong dephasing is completely defined by values of two parameters W and Γ. The method of their evaluation is discussed in the second part of the section.

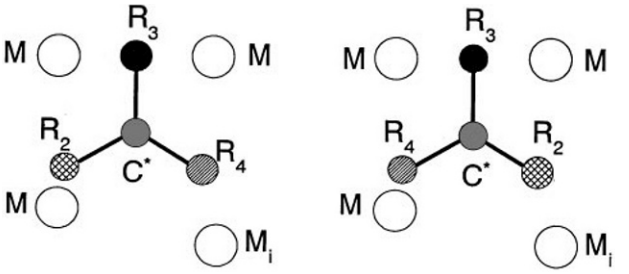

Fig. 2. Top view of mirror antipodes of a chiral molecule in the elementary cell of a disordered solid. A chiral molecule has four different ligands $R_1, R_2, R_3,$ and R_4 bound to the central carbon atom C^*. The ligand R_1 is located above C^* and cannot be seen on the figure. The elementary cell of a disordered solid is formed by species M. One of them, M_i, occupies the irregular position. The asymmetry, E_0, of energy levels corresponding to the L- and D-states arises due to the distinct local interaction of ligands R_2 and R_4 with their nearest neighbours M and M_i. Note that for a perfect square lattice this distinction disappears and E_0 becomes equal zero

2.1 *Kinetic analysis*

Our approach to the kinetic description of DWS is based on the Bloch equation for the density matrix $\hat{\rho}(t)$. In the temperature range under investigation the elements $\rho_{\alpha\beta}$ of this matrix satisfy a set of equations

$$\begin{aligned}
\frac{\partial\rho_{11}}{\partial t} &= -\frac{i}{2\hbar}\Omega(\rho_{21}-\rho_{12}) - W(\rho_{11}-\tfrac{1}{2}),\\
\frac{\partial\rho_{22}}{\partial t} &= \frac{i}{2\hbar}\Omega(\rho_{21}-\rho_{12}) - W(\rho_{22}-\tfrac{1}{2}),\\
\frac{\partial\rho_{12}}{\partial t} &= (iE_0/\hbar-\Gamma)\rho_{12} - i\Omega(\rho_{22}-\rho_{11})/2,\\
\frac{\partial\rho_{21}}{\partial t} &= (-iE_0/\hbar-\Gamma)\rho_{21} + i\Omega(\rho_{22}-\rho_{11})/2.
\end{aligned} \tag{3}$$

Here subscripts α and β have values 1 or 2 which correspond to the "left" and "right" wells of DWS, respectively. Since for the sake of definiteness we have assumed that at $t = 0$ only the L-state is occupied, (3) should be solved under the initial conditions

$$\rho_{22}(0) = \rho_{12}(0) = \rho_{21}(0) = 0, \quad \rho_{11}(0) = 1. \tag{4}$$

To characterize the dynamics of transitions within DWS, we introduce the difference $\Delta\rho(t)$ in probabilities to find a particle in the "left" and "right" wells. Then the use of the Laplace transform $\tilde{\rho}_{\alpha\beta} = \int_0^\infty \rho_{\alpha\beta}\exp(-st)\,\mathrm{d}t$ for solving (3), enables one to express this quantity as

$$\Delta\tilde{\rho} = \tilde{\rho}_{11} - \tilde{\rho}_{22} = \left[s + W + \frac{(s+\Gamma)\Omega^2}{(s+\Gamma)^2 + E_0^2/\hbar^2} \right]^{-1}. \quad (5)$$

For an isolated DWS, parameters E_0, W, Γ are equal to zero, and the inverse Laplace transform of (5) gives the familiar result (see e.g. [16]).

$$\Delta\rho(t) = \cos(\Omega t). \quad (6)$$

Being applied to a chiral molecule, it shows that in the absence of the interaction with the medium the transition between two mirror antipodal states follows the pattern typical for coherent tunnelling oscillations. This is also true as long as a chiral molecule is not coupled with phonons. Indeed, if such a molecule is imbedded in the irregular rigid lattice, both W and Γ equal zero as before, but $E_0 \neq 0$. As a consequence, the inverse Laplace transform of (5) yields

$$\Delta\rho(t) = (E_0/E)^2 + (\hbar\Omega/E)^2\cos(Et/\hbar), \quad (7)$$

where E denotes the total splitting energy defined as

$$E = (E_0^2 + \hbar^2\Omega^2)^{1/2}. \quad (8)$$

The comparison of (7) with (6) shows that similar to the time behavior of the isolated DWS, dynamics of transitions within such a system embedded in a rigid matrix exhibits coherent oscillations. The only distinction between two cases is a smaller amplitude of the oscillations in the asymmetric situation. According to (7), for $E_0 \gg \hbar\Omega$ its value becomes so small that a chiral molecule in a rigid lattice appears to be predominantly localized in the initial isomeric form.

However, it should be noted that the above explanation of the Hund paradox is incomplete since it ignores the effect of phonons on the dynamics of DWS. Such an effect becomes evident from the analysis of (5) in the limit of the weak DWS-phonon coupling, where both W and Γ are much less than $E/\hbar$. Under these conditions the time dependence of $\Delta\rho$ becomes distinct from that expected from (7), i.e.

$$\Delta\rho = (E_0/E)^2\exp(-W_{12}t) + (\hbar\Omega/E)^2\cos(Et/\hbar)\exp(-\Gamma t) \quad (9)$$

where W_{12} is the total rate of tunnelling transitions given by

$$W_{12} = W + \frac{\hbar^2\Omega^2\Gamma}{E_0^2 + \hbar^2\Gamma^2}. \quad (10)$$

Equation (9) implies that the inclusion of the weak interaction between a single chiral molecule and phonons leads to the damping of coherent oscillations between the L- and the D-state in conformity with earlier theoretical findings [9–11]. Such an oscillatory motion is suppressed in the strong coupling limit, where $\Gamma \gg E/\hbar \geq \Omega$. In the latter case $\Delta\rho(t)$ evaluated from (5) varies with time following the exponential law

$$\Delta\rho(t) = \exp(-W_{12}t), \quad (11)$$

which corresponds to the complete dephasing.

The obtained result suggests the alternative explanation of the Hund paradox that does not require any special assumptions about the energy asymmetry of the L- and D-states in a rigid matrix. This explanation lies in the fact that the strong coupling of a chiral molecule with phonons makes the transitions between these states irreversible due to a loss of the phase coherence. Nevertheless, the kinetic analysis alone cannot offer the answer to the question as to whether the strong DWS-phonon interaction provides the stabilization of molecular chiral states. To resolve the latter question, it also needs to be ascertained if such an interaction indeed yields the dephasing rates sufficient for a complete loss of coherence. This calls for a method which makes it possible to calculate the kinetic parameters appearing in (11). Such a method, taking into account both a single- and a multi-phonon processes, will be considered below.

2.2 *Evaluations of kinetic parameters*

The Hamiltonian of the system under consideration has the form

$$\hat{H} = \hat{H}_0 + \hat{H}_{ph} + \hat{H}_{int}, \quad (12)$$

where $\hat{H}_0$, $\hat{H}_{int}$, and $\hat{H}_{ph}$ describe DWS in a rigid lattice, a phonon thermostat, and the interaction of DWS with phonon gas, respectively. Using the site representation, we express three terms of (12) as follows

$$H_0 = E_0(d_1^+d_1 - d_2^+d_2)/2 + \hbar\Omega(d_1^+d_2 + d_2^+d_1)/2\,, \quad (13)$$

$$\hat{H}_{ph} = \sum_{\{\mathbf{k},j\}} \hbar\omega_{\mathbf{k},j} b^+_{\mathbf{k},j} b_{\mathbf{k}j}\,, \quad (14)$$

$$\hat{H}_{int} = \sum_n \hat{V}_n (d_1^+d_1 - d_2^+d_2). \quad (15)$$

Here d_i^+ and d_i are the creation and annihilation operators for a chiral molecule in the i-th state with i being equal to 1 and 2 for the "left" and "right" wells as before, $b^+_{\mathbf{k}j}$ and $b_{\mathbf{k},j}$ are the same operators, but for phonons which belong to the branch j and have the wave vector $\mathbf{k}$, $\omega_{\mathbf{k},j} = c_s^j k$ is the frequency of the j-th phonon mode ($j = 1, 2, 3$) , c_s^j is the sound velocity for the j-th mode, and $\hat{V}_n$ is the Hamiltonian of the n-th order phonon process.

Since the operator $\hat{V}_n$ can, in principle, be specified for any $n \geq 1$, the Fermi Golden rule allows the evaluation of the contributions Γ_n made by each one of phonon processes into the dephasing rate. The contribution arising due to a single phonon process deserves special attention. The point is that this process must be accompanied by tunnelling between two levels since there is no way to absorb or to emit a single phonon without a subbarrier transition; otherwise the phonons with a zero frequency would be required. However, phonons with $\omega = 0$ are actually absent in the system because the appropriate density of states depends on the frequency as ω^2. As a consequence, a single phonon process always results in the transition between L- and D-states with the rate approximated by

$$W = 2\Gamma_1 = \frac{\Omega^2}{E^2}\int_{-\infty}^{+\infty} \langle \hat{V}_1(t)\hat{V}_1(0)\rangle \exp(iE_0 t)\,\mathrm{d}t, \tag{16}$$

where the notation $\langle \ldots \rangle$ means averaging over the ensemble of states of the phonon subsystem in a thermal equilibrium.

The above restriction does not exist for a multi-phonon "scattering". In this case the major contribution to the dephasing rate comes from the processes without tunnelling [16, 35], so that for $n \geq 2$ the Fermi Golden Rule gives

$$\Gamma_n = \frac{1}{2}\int_{-\infty}^{+\infty} \langle \hat{V}_n(t)\hat{V}_n(0)\rangle \mathrm{d}t. \tag{17}$$

Now the calculation of the dephasing is straightforward and reduces to the summation of all contributions, namely

$$\Gamma = \sum_{n=1}^{\infty} \Gamma_n. \tag{18}$$

The second physical parameter which controls the dynamics of DWS in the strong coupling limit (cf. (11)) is the total transition rate for tunnelling W_{12}. According to (10), this rate is expressed in terms of Γ, W, and Ω. Hence (16), (17), and (18) together with (10) define the tunnelling transition rate if the Ω value is known.

In order to illustrate the application of the method proposed here for calculating Γ and W, in the next section we specify the Hamiltonian for single and multi-phonon processes and calculate their contributions in the rate of tunnelling and in the dephasing rate. This allows us to show that for $T < \theta_D$ these rates are mainly determined by one- and two-phonon scattering. The temperatures ranges where both processes dominates are also estimated.

3 Tunnelling and dephasing rates: single- and multi-phonon contributions

3.1 Single-phonon process

In this case the Hamiltonian $\hat{V}_1$ for the DWS-phonon interaction can be written as

$$\hat{V}_1 = i\sum_{j,\mathbf{k}} k_B\theta_D[\hbar/(Mc_s^jN)]^{1/2}k^{1/2}\xi_{\mathbf{k},j}(b_{\mathbf{k},j}^{+} - b_{\mathbf{k},j}), \tag{19}$$

where N is the total number of elementary cells of mass M and $\xi_{\mathbf{k},j}$ is the coupling constant for phonons which belong to the branch j and have the wave vector $\mathbf{k}$. The factor $k^{1/2}$ appears in (19) due to the translation invariance of DWS and its molecular environment.

The substitution of (19) into (16) yields

$$W = \frac{(\hbar\Omega k_B\theta_D)^2}{NME^2}\sum_j\sum_{\mathbf{k}} (\xi_{\mathbf{k},j}^2/c_s^j)k\delta(E - \hbar c_s^j\mathbf{k})\,(2\nu_E + 1), \tag{20}$$

where $\nu_E = [\exp(E/k_BT) - 1]^{-1}$ is the occupation number for phonons with energy E. Taking into account that in (20) summation over k can be replaced by integration and making evident transformations, we arrive at the following expression for the incoherent tunnelling rate

$$W = 2\Gamma_1 = \frac{9\pi}{\hbar}\xi_0^2\frac{(\hbar\Omega)^2E}{Mc_s^2k_B\theta_D}\coth[E/(2k_BT)], \tag{21}$$

with $\xi_0/c_s^5 = (1/3)\sum_j \xi_{0,j}^2/(c_j^s)^5$ and $\xi_{0,j}$ being the DWS-phonon coupling constant for the wave vector $k_j = E/(\hbar c_s^j)$. Since $(k_B\theta_D/\hbar)^3 = 6\pi^2c_s^3/V$, (21) is identical to the expression for W obtained in earlier publications [12, 36].

3.2 Contributions of multi-phonon processes

To evaluate the contribution made by multi-phonon processes into the values of parameters Γ and W, we start with the two-phonon Hamiltonian defined by

$$\hat{V}_2 = -\frac{k_B\theta_D\hbar}{NM}\sum_{j,j',\mathbf{k}',\mathbf{k}} (c_s^jc_s^{j'})^{-1/2}(kk')^{1/2}\xi_{\mathbf{k},\mathbf{k}}^{j,j'} \times (b_{\mathbf{k},j}^{+} - b_{\mathbf{k},j})(b_{\mathbf{k}',j'}^{+} - b_{\mathbf{k}',j'}). \tag{22}$$

The most significant contribution of two-phonon processes is usually associated with scattering [16]. Hence

$$\Gamma_2 = \left(\frac{k_B\theta_D}{NM}\right)^2\sum_{j,j'}\frac{1}{c_s^jc_s^{j'}}\sum_{\mathbf{k},\mathbf{k}'} kk'(\xi_{\mathbf{k},\mathbf{k}'}^{j,j'})^2\nu_{\mathbf{k},j} \times (1 + \nu_{\mathbf{k}',j'})\delta(\omega_{\mathbf{k},j} - \omega_{\mathbf{k}',j'}), \tag{23}$$

where $\nu_{\mathbf{k},j} = [\exp(\hbar\omega_{\mathbf{k},j}/k_BT) - 1]^{-1}$.

It should be mentioned that $\xi_{\mathbf{k},\mathbf{k}'}^{j,j'}$ arising in (23) is proportional to the scattering amplitude. The latter quantity has a maximum value for events with small changes of wave vector $\Delta k = |\mathbf{k} - \mathbf{k}'| < 1/R_s$ because of a finite size of a molecular scatterer. In order to take this circumstance into account, we assume that

$$(\xi_{\mathbf{k},\mathbf{k}'}^{j,j'})^2 = \xi_0\exp[-(\mathbf{k} - \mathbf{k}')^2R_s^2] \tag{24}$$

and then substitute (24) into (23). As a result, two limiting cases become evident. For temperatures exceeding $T_0 = \hbar c_s/(k_BR_s) \sim \theta_D(a/R_s)$ that correspond to the short wavelength limit ($\lambda_{th} < R_s$), the contribution of the two-phonon process in the dephasing rate is given by

$$\Gamma_2 \cong 10^4k_B\theta_D(T/\theta_D)^5\,[k_B\theta_D\xi_0/(Mc_s^2)]^2(a/R)^2/\hbar\,, \tag{25}$$

where a is the size of the elementary cell. Otherwise (i.e. for $T < T_0$) one gets

$$\Gamma_2 \cong 10^5k_B\theta_D(T/\theta_D)^7[k_B\theta_D\xi_0/(Mc_s^2)]^2/\hbar \tag{26}$$

in agreement with the expression available in the literature (see e.g. [16]) for the rate of the two-phonon dephasing in the long wavelength limit ($\lambda_{th} > R_s$). Note that large numerical factors in (25) and (26) result from the integration of the polynomial function k^m with the high value of the exponent m.

Contributions Γ_n coming from the phonon process of higher order can be evaluated in similar fashion. As an example we present the result obtained for the three-phonon inelastic scattering. Such process is described by the Hamiltonian

$$\hat{V}_3 = -i\frac{k_B\theta_D\hbar^{3/2}}{(NM)^{3/2}} \sum_{j,j',j''} \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} (c_s^j c_s^{j'} c_s^{j''})^{-1/2}(kk'k'')^{1/2} \xi_{\mathbf{k},\mathbf{k}',\mathbf{k}''}^{j,j',j''}$$

$$\times (b_{\mathbf{k},j}^+ - b_{\mathbf{k},j})(b_{\mathbf{k}',j'}^+ - b_{\mathbf{k}',j'})(b_{\mathbf{k}'',j''}^+ - b_{\mathbf{k}'',j''}). \qquad (27)$$

Calculations similar to those made for the two-phonon scattering again shows the existence of low-temperature (short wavelength) and high-temperature (long wavelength) limits

$$\Gamma_3 \cong 10^5 \frac{(k_B\theta_D)^4 \xi_0^2}{\hbar(Mc_s^2)^3} (T/\theta_D)^8 \begin{cases} (a/R_s)^3 & \text{if } T > T_0 \\ 10^2(T/\theta_D)^3 & \text{if } T < T_0 \end{cases}. \qquad (28)$$

However, a comparison of (28) with (25, 26) shows that Γ_3 depends on temperature much stronger than Γ_2. Taking typical values of parameter appearing in (25), (26), and (28), one can easily verify that for $Mc_s^2 \sim 10$ eV and $k_B\theta_D \sim 0.01$ eV the dephasing rate related to the two-phonon scattering is higher than Γ_3 as long as T is below $\theta_D \sim 100$ K. This implies that for $T < \theta_D$ the contribution of the three-phonon process in the dephasing rate can be neglected. For each one of the processes with the number of phonons $n > 2$, the dephasing rate will be even lower than Γ_3 since any additional phonon involved in the single scattering event decreases the phase volume at least by a factor $(T/\theta_D)^3 \ll 1$. Besides, any extra phonon adds the small factor $k_B\theta_D/(Mc_s^2) \sim 10^{-3}$ in the corresponding Γ_n value. Thus, one- and two-phonon processes make the main contribution in the dephasing rate below the Debye temperature.

4 Discussion and conclusions

In the present paper we consider the Hund paradox of optical isomers [1] and propose its explanation in terms of the strong coupling between a single chiral molecule modeled by DWS and the phonon surroundings. The analysis of the DWS dynamics in low-temperature solids (see Sect. 2) enables us to show that such a coupling can lead to the complete dephasing which, in turn, suppresses coherent tunnelling oscillations between the "left" and "right" wells. As a result, transitions between mirror-antipodal states which are reversible in time for an isolated chiral molecule (cf. (6)) become irreversible for the same molecule embedded in low-temperature solid (cf. (11)). In this regard molecular chiral states turn out to be stabilized by the medium.

The above mechanism of stabilization works only if phonon processes with the dephasing rate higher than $E/\hbar$ exist. According to numerical estimations carried out using (21) with $Mc_s^2 \sim 10$ eV, $k_B\theta_D \sim 0.01$ eV and $\Omega \sim 10^7$ s^{-1}, a single-phonon process cannot be considered as an appropriate candidate since for $T < \theta_D$ its contribution to the dephasing rate is too small in comparison with $E/\hbar$. However calculations made for the two-phonon scattering invoking (26) with the same value of parameters Mc_s^2 and $k_B\theta_D$ show that for typical coupling constant $\xi_0 \sim 100$ [37] the two-phonon scattering will provide the sufficient dephasing rate above the temperature T^* given by

$$T^* \cong 0.01\theta_D[E/(\hbar\Omega)]^{1/7}. \qquad (29)$$

For the symmetric DWS, $E \cong \hbar\Omega$ (see (8)) and from (29) we get $T^* \sim 1$ K. The result for the asymmetric situation is almost the same because T^* depends only slightly on E in view of (29). In spite of small differences, in both cases the estimated T^* are much below T_0 obtained for reasonable values of the ratio a/R_s ranging from 0.1 to 1. Taking this circumstance into account, we conclude that the dephasing caused by two-phonon scattering stabilizes molecular chiral states in solids with a temperature less than θ_D, but higher than a few Kelvin degrees.

It appears to be important that the proposed mechanism of stabilization becomes efficient under physical conditions typical for molecules of organic compounds found [21–24] in the dirty ice mantles around the cores of the dust particles in dense interstellar clouds. The temperature of these grains is estimated as $T_g \cong 20$ K [18, 24] and hence falls within the temperature range where the two-phonon dephasing is the main stabilizing factor for molecular chiral states. Setting $T = T_g$ in (21), (25), (26) and using the above values of the other parameters, we obtain that at 20 K the incoherent tunnelling rate is lower than the frequency of coherent tunnelling by four orders of magnitude ($W = 2\Gamma_1 \sim 10^3$ s^{-1}), whereas $\Gamma_2 \sim 10^{12}$ s^{-1} and exceeds Ω by five orders of magnitude. By virtue of (10) this implies that for the discussed conditions the rate of the subbarrier transitions between two chiral states are completely controlled by incoherent tunnelling rather than by free tunnelling oscillations with the frequency given by (2). As a consequence, the decay of the population difference $\Delta\rho(t)$ can be considered as exponential with the rate constant equal to W.

Summing up, we conclude that the two-phonon dephasing arising from the interaction of a chiral molecule with a low-temperature solid removes the Hund's paradox without invoking the non-linear wave mechanics [3, 14]. In addition, such a dephasing provides the efficient mechanism for stabilization of molecular chiral states which preserve the certain "sign" of chirality over the time scale comparable with the rates of low-temperature physical and chemical processes. This circumstance makes the question about the possibility of a mirror symmetry in the cold prehistory of life accessible for analysis by means of modern methods of chemical physics [17, 18, 25].

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