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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Supplementary Information

Time evolution of several properties (N=100 unless otherwise indicated)

Figure s1. Comparison between the (j=0, m_j=0) and (j=2, m_j=0) populations of T_2@HeND obtained from the relaxation dynamics and the results derived from a sigmoid function fitting of the (j=0, m_j=0) population.

Figure s2. Expected value of $\hat{j}^2$ for the (j=0, m_j=0)←(j=2, m_j=0) relaxation of the molecules in HeND, as a function of time.

Figure s3. Helium radial density of T_2(j=2, m_j=0)@HeND along the x, y and z-axes, as a function of time.

Figure s4. Snapshots of the helium density in the xy-plane for T_2(j=2, m_j=0)@HeND, as a function of time.

Table s1. Coupling terms squared values between the rotational states of the molecules in HeND, including those of T_2 with HeNDs of different sizes.

Figure s5. Relaxation of the (j=2, m_j=0) state of the molecules in HeND: inverse of the relaxation time properties *vs.* $1/B_e$; inverse of the relaxation time properties relative to those of Sx_2 *vs.* B_e.

Figure s6. Relaxation of T_2(j=2, m_j=0) in HeND: populations of the (j=2, m_j=0) and (j=0, m_j=0) states; components of the helium energy; T_2-helium interaction energy; V_{ij} coupling term between the two states.

Figure s7. Expected value of $\widehat{j^2}$ for Sx_2 in HeND at three different initial excitations, (j_o, m_{jo}=0): (2, 0), (4, 0) and (6, 0), as a function of time.

Figure s8. Relaxation of T_2(j=2, m_j=0) in HeNDs of different sizes: inverse of the relaxation time properties *vs.* average V_{ij}^2; average V_{ij}^2 *vs.* T_2-helium interaction energy; T_2-helium interaction energy *vs. N.*
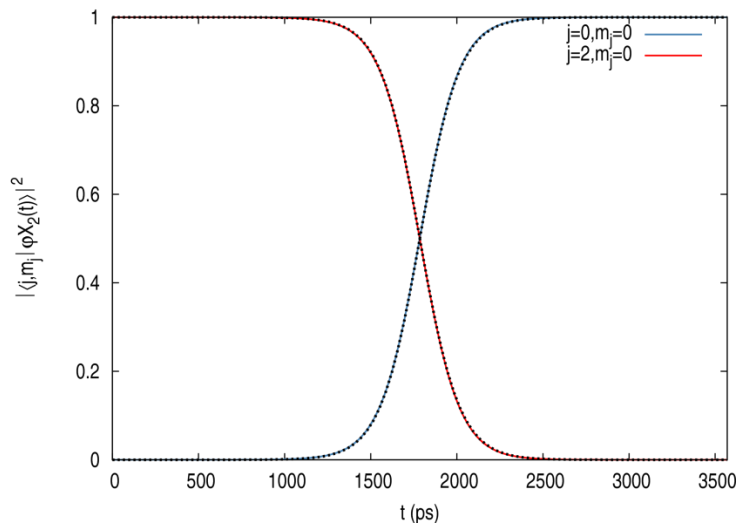
Figure s1. Comparison between the time evolution of the (j=0, m_j=0) and (j=2, m_j=0) populations for the $T_2@(^4He)_{100}$ nanodroplet obtained from the relaxation dynamics (blue and red lines, respectively) and the results derived from a sigmoid function fitting of the (j=0, m_j=0) populations.
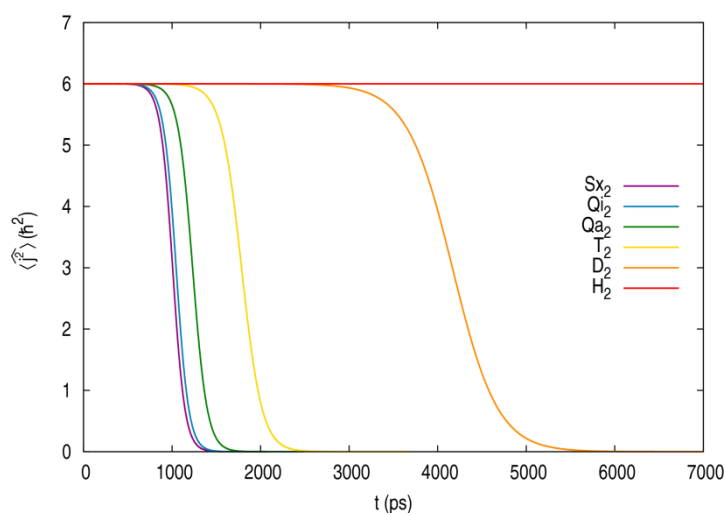
Figure s2. Expected value of $\hat{j}^2$ for the (j=0, m_j=0)←(j=2, m_j=0) relaxation of the molecules in $(^4He)_{100}$, as a function of time.
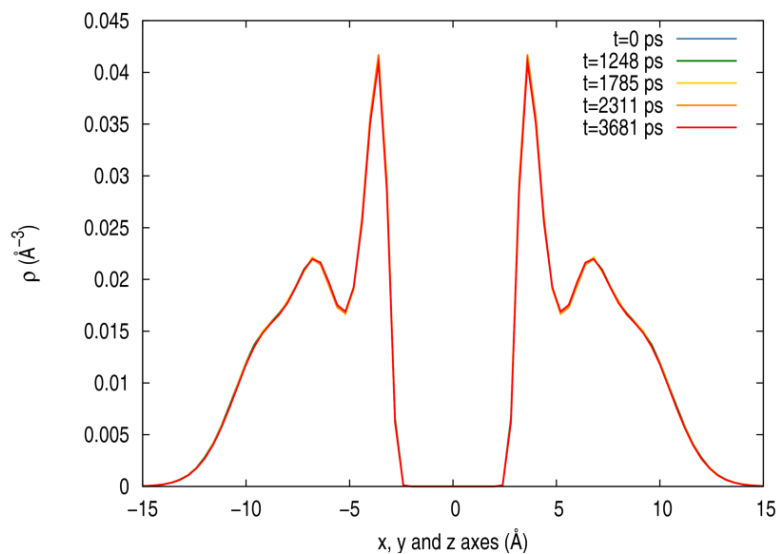
Figure s3. Helium radial density of the $T_2(j=2, m_j=0)@(^4He)_{100}$ nanodroplet along the x, y and z-axes, as a function of time. The time values of 0, 1785 and 2311 ps correspond to the initial excitation, lifetime and global relaxation time of the molecule, respectively (cf. Table 1).
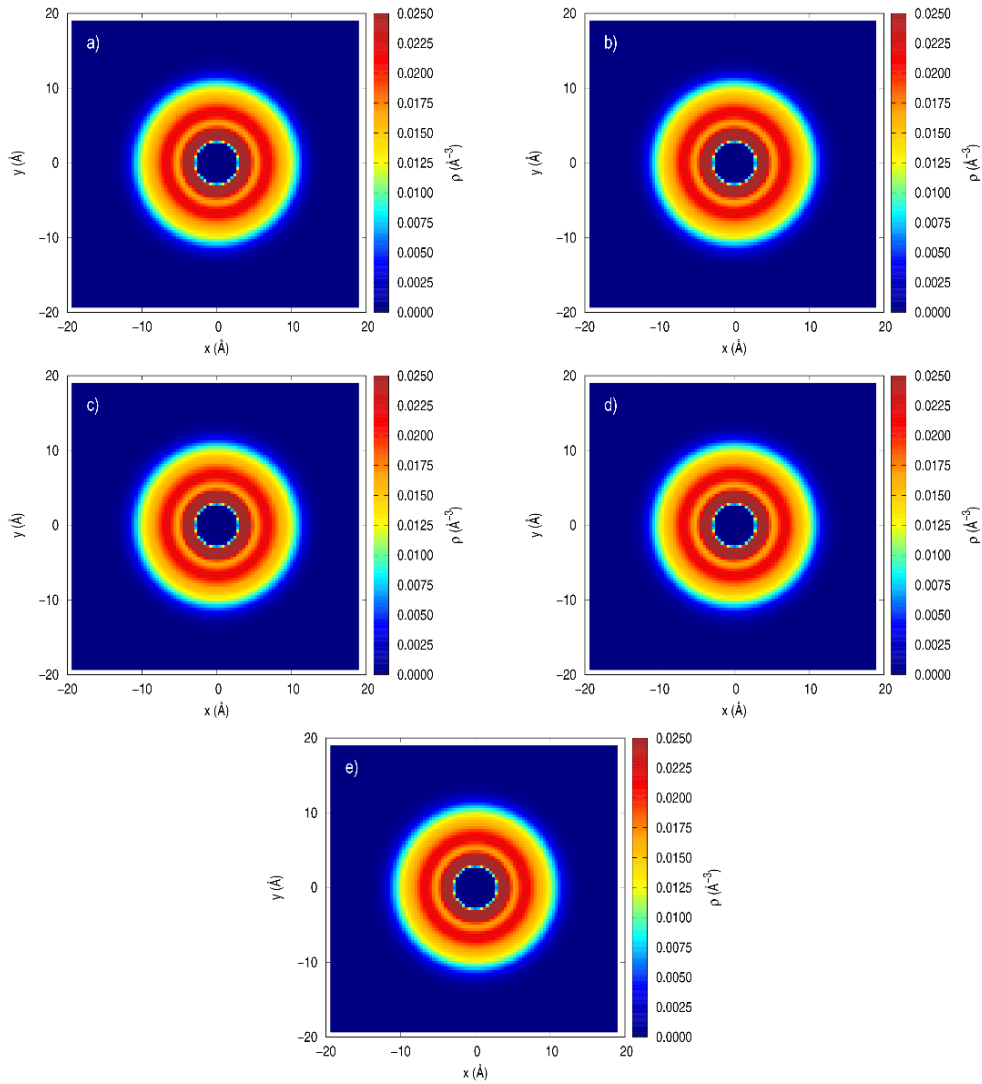
Figure s4. Snapshots of the helium density in the xy-plane for the $T_2(j=2, \; m_j=0)@(^4He)_{100}$ nanodroplet, as a function of time. The same time values as in Figure s3 are considered ($t=0$, 1248, 1785, 2311 and 3681 ps for (a), (b), (c), (d) and (e), respectively).

Table s1. Coupling terms squared values (in K^2) between the rotational states.[a]

Relaxation from $j=2, m_j=0$ to $j=0, m_j=0$

	V_{ij}^2 initial	V_{ij}^2 average	V_{ij}^2 max	V_{ij}^2 min	t(p=0.99)	t(p=0.01)	N points
D_2	1.43 E-03	3.23E-03	9.98E-03	4.73E-04	2972	5334	1576
T_2	1.43E-03	3.42E-03	1.01E-02	2.99E-04	1248	2310	709
Qa_2	1.43E-03	3.37E-03	1.23E-02	4.45E-05	849	1606	506
Qi_2	1.43E-03	3.45E-03	1.45E-02	1.34E-07	715,5	1369	437
Sx_2	1.42E-03	3.29E-03	1.58E-02	2.38E-08	685,5	1320	424

Several relaxations of Sx_2 ($j_0, m_{j0}=0$)

		V_{ij}^2 initial	V_{ij}^2 average	V_{ij}^2 max	V_{ij}^2 min	t(p=0.99)	t(p=0.01)	N points
$j_0=2$	0←2	1.42E-03	3.29E-03	1.58E-02	2.38E-08	685.5	1320	424
$j_0=4$	0←2	1.73E-03	3.35E-03	1.69E-02	1.01E-08	3564	4253	459
	2←4	4.24E-02	4.18E-02	5.20E-02	3.24E-02	1839	3564	1150
$j_0=6$	0←2	1.80E-03	3.65E-03	2.43E-02	5.34E-09	11532	12297	510
	2←4	4.26E-02	4.10E-02	6.35E-02	2.51E-02	9760	11532	1184
	4←6	1.25E-01	1.25E-01	1.53E-01	1.01E-01	4990	9760	3188

Relaxation from $j=2, m_j=0$ to $j=0, m_j=0$ for T_2

N	V_{ij}^2 initial	V_{ij}^2 average	V_{ij}^2 max	V_{ij}^2 min	t(p=0.99)	t(p=0.01)	N points
25	7.01E-04	1.95E-03	5.99E-03	1.43E-04	1609	2927	879
50	1.11E-03	2.81E-03	8.26E-03	2.59E-04	1356	2495	760
75	1.32E-03	3.11E-03	9.18E-03	3.24E-04	1290	2380	728
100	1.43E-03	3.42E-03	1.01E-02	2.99E-04	1248	2310	709
125	1.50E-03	3.54E-03	1.02E-02	3.76E-04	1228	2278	701

[a] The V_{ij} coupling terms are real numbers. The reported initial values correspond to the value at t=0, that is after the sudden rotational excitation. They essentially coincide with the values at the propagation time where the population of the excited state is equal to 0.99. In this table are also indicated the time values at which the population of the excited state is equal to 0.99, t(p=0.99), and 0.01, (t(p=0.01)), where the time is given in ps. *N* points indicates the number of propagation times considered when analyzing the data in the corresponding time interval.
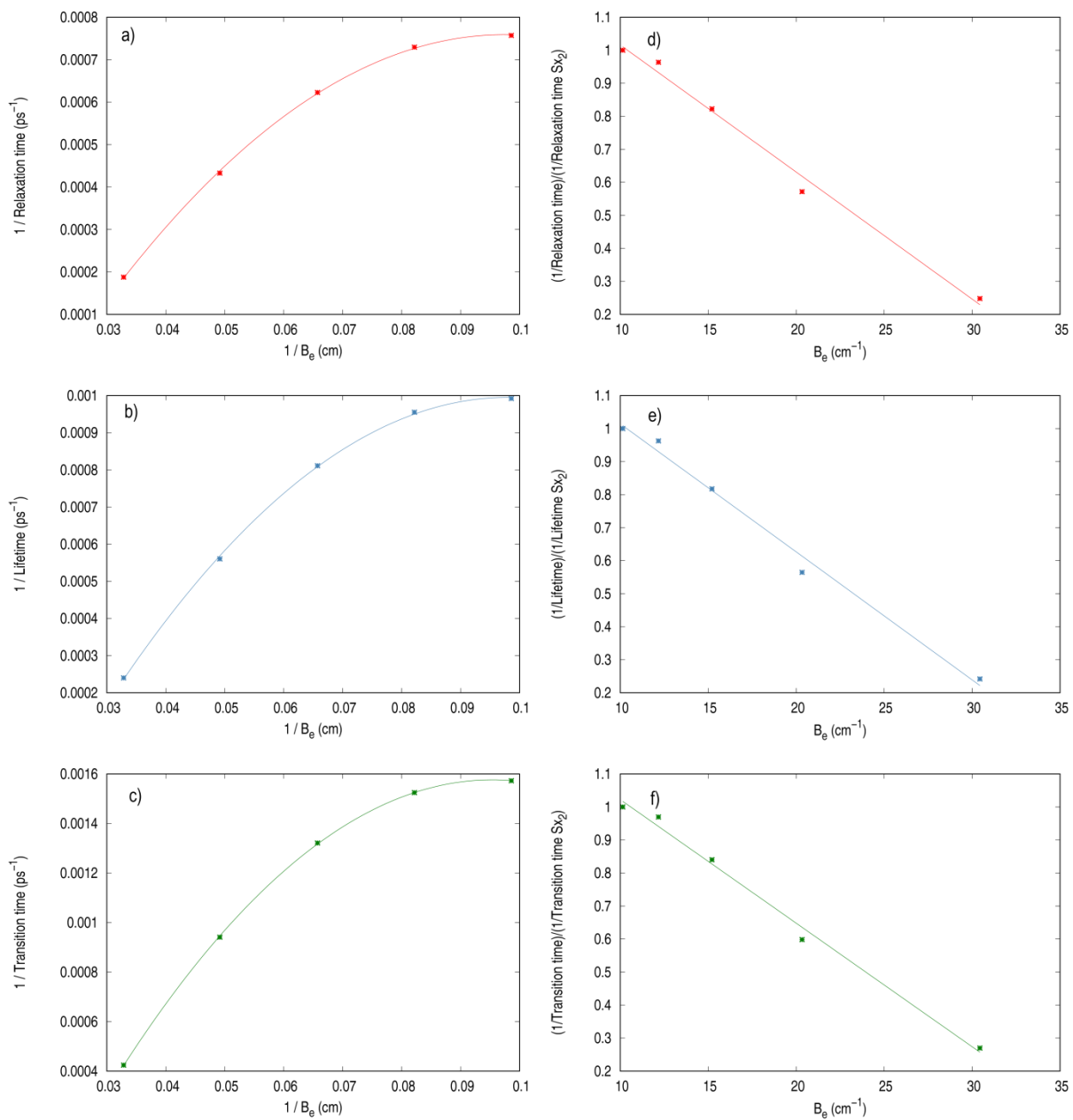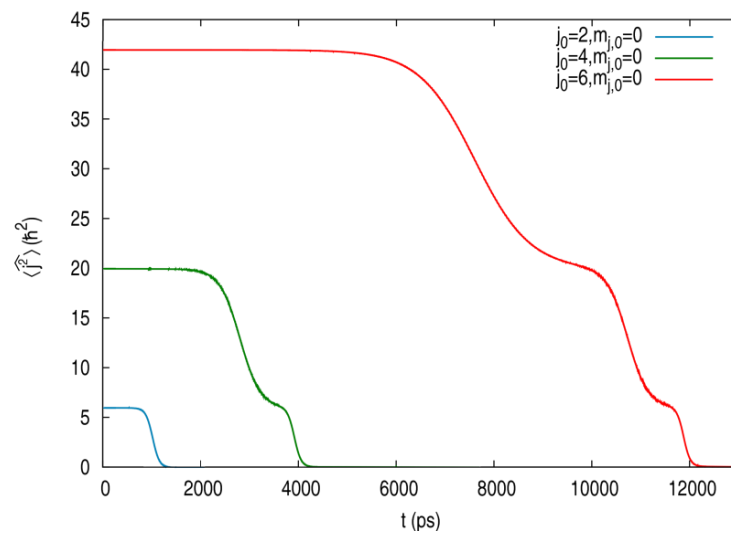
Figure s5. Relaxation of the (j=2, m_j=0) state of the molecules in (^{4}He)$_{100}$. Inverse of the relaxation time properties (global relaxation time (a), lifetime (b) and transition time (c)) *vs.* 1/B_e. Moreover, the previous inverse values, taken with respect to the corresponding inverse values of Sx_2, *vs.* B_e (d-f, respectively) are also given.
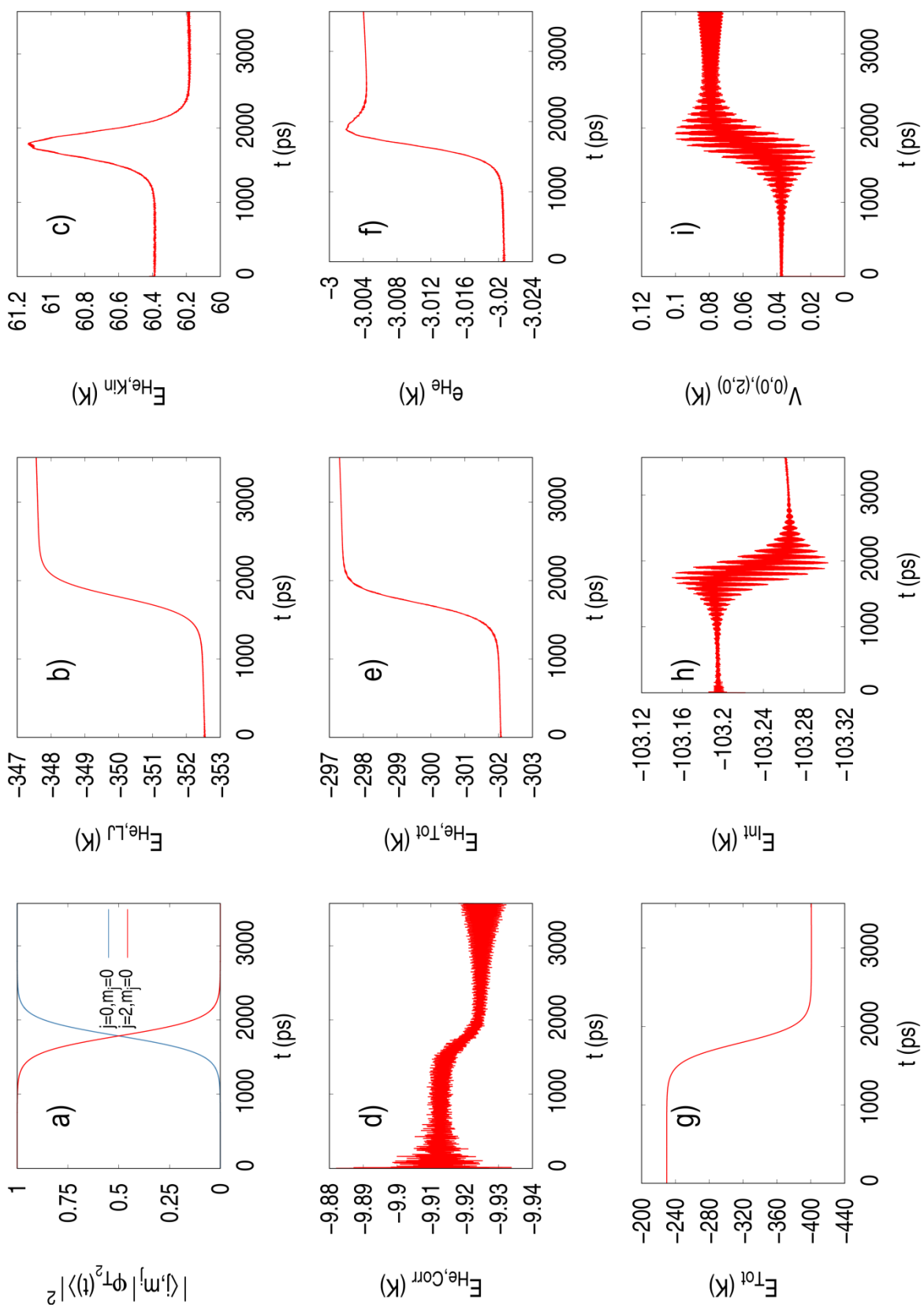
Figure s6. Relaxation of T_2 ($j=2$, $m_j=0$) in (^{4}He)$_{100}$: (a) populations of ($j=2$, $m_j=0$) and ($j=0$, $m_j=0$); (b) potential energy of helium; (c) kinetic energy of helium; (d) correlation energy of helium; (e) energy of helium (sum of the previous three energy terms); (f) energy per helium atom of the HeND; (g) energy of the doped HeND; (h) interaction potential energy T_2-helium; (i) V_{ij} coupling term between ($j=2$, $m_j=0$) and ($j=0$, $m_j=0$). Please, note the different energy scales.

Figure s7. Expected value of $\widehat{j}^2$ for Sx_2 in $(^4He)_{100}$ at three different initial excitations, $(j_o, m_{jo}=0)$: (2, 0), (4, 0) and (6, 0), as a function of time.
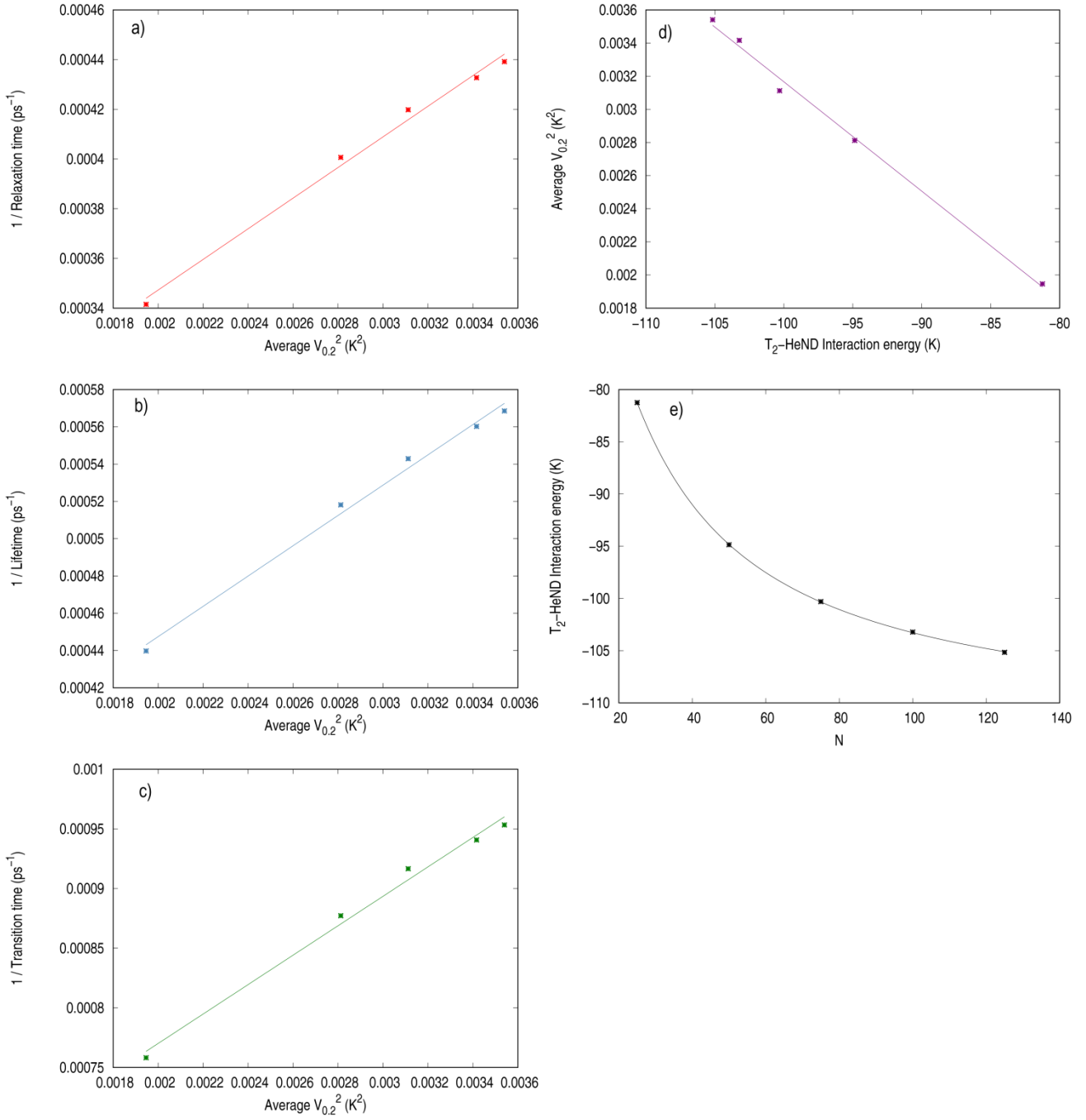
Figure s8. Relaxation of $T_2(j=2, m_j=0)$ in HeNDs of different sizes. Inverse of the relaxation time properties (global relaxation time (a), lifetime (b) and transition time (c)) *vs.* the average V_{ij}^2. Moreover, the average V_{ij}^2 *vs.* the T_2-helium interaction energy (d) and the T_2-helium interaction energy *vs.* N (e) are also given.