

## Intramolecular vibrational relaxation seen as expansion in phase space. III. The long-time limit

V. B. Pavlov-Verevkin and J. C. Lorquet

Citation: *The Journal of Chemical Physics* **107**, 6677 (1997); doi: 10.1063/1.474910

View online: <http://dx.doi.org/10.1063/1.474910>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/107/17?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Intramolecular vibrational energy redistribution as state space diffusion: Classical-quantum correspondence](#)  
*J. Chem. Phys.* **125**, 141101 (2006); 10.1063/1.2358138

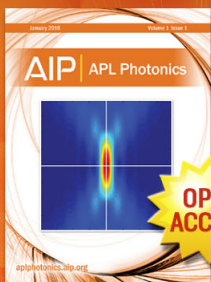
[Intramolecular energy transfer in highly vibrationally excited methanol. II. Multiple time scales of energy redistribution](#)  
*J. Chem. Phys.* **110**, 11346 (1999); 10.1063/1.479075

[Vibrational relaxation of azide ion in water: The role of intramolecular charge fluctuation and solvent-induced vibrational coupling](#)  
*J. Chem. Phys.* **109**, 5511 (1998); 10.1063/1.477170

[The short-time intramolecular dynamics of solutes in liquids. II. Vibrational population relaxation](#)  
*J. Chem. Phys.* **107**, 3098 (1997); 10.1063/1.474664

[From the sparse to the statistical limit of intramolecular vibrational redistribution in vibrational predissociation: ArCl 2 as an example](#)  
*J. Chem. Phys.* **107**, 1406 (1997); 10.1063/1.474495

---



Launching in 2016!  
The future of applied photonics research is here

OPEN  
ACCESS

**AIP** | APL  
Photonics

# Intramolecular vibrational relaxation seen as expansion in phase space.

## III. The long-time limit

V. B. Pavlov-Verevkin<sup>a)</sup> and J. C. Lorquet<sup>b)</sup>

Département de Chimie, Université de Liège, Sart-Tilman (B6), B-4000 Liège 1, Belgium

(Received 14 April 1997; accepted 30 July 1997)

Asymptotic formulas that describe the behavior of the function  $N(T)$  measuring the phase space volume sampled by a nonstationary wave packet during its time evolution are derived. It is shown that, in the long-time limit,  $N(T) \sim T^{-1}$  when the dynamics is regular, whereas  $N(T) \sim T^{-2} \ln T$  for the chaotic case. © 1997 American Institute of Physics. [S0021-9606(97)03641-6]

### I. INTRODUCTION

Intramolecular vibrational relaxation is a process of fundamental importance in the theory of unimolecular reactions. The concept of autocorrelation function, derived from the Fourier time transform of an optical spectrum, has been of great help in its study<sup>1-19</sup>

$$C(t) = \int_{-\infty}^{+\infty} I(E) \exp(-iEt/\hbar) dE, \quad (1)$$

where  $I(E)$  is the spectral function, given in principle by

$$I(E) = \sum_n p_n \delta(E - E_n), \quad (2)$$

where  $p_n$  are the usual Franck-Condon factors. The square modulus of  $C(t)$  is sometimes called the survival probability,

$$|C(t)|^2 = \sum_{n,m} p_n p_m \cos(\omega_{nk}t), \quad (3)$$

with

$$\omega_{nk} = (E_n - E_k)/\hbar. \quad (4)$$

These functions have been used by Heller<sup>3</sup> to evaluate the volume in phase space sampled during the evolution of a nonstationary wave packet up to time  $T$ . Denoting by  $N(T)$  the number of cells sampled as a function of time, the following expression can be derived:<sup>6</sup>

$$N(T)^{-1} = \sum_k p_k^2 + 2S(T), \quad (5)$$

where

$$S(T) = \sum_{n=1} p_n \sum_{k=n+1} p_k [\sin(\omega_{nk}T/2)/(\omega_{nk}T/2)]^2. \quad (6)$$

The function  $N(T)$  is seen to increase from an initial value of 1 at  $T=0$  to a final value  $N_\infty$  given by<sup>3,6</sup>

<sup>a)</sup>Permanent address: Chemistry Department, Moscow State University, Moscow 119899, Russia.

<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: U211101@avml.ulg.ac.be; Fax: 32-4-3662933.

$$N_\infty = \left( \sum_k p_k^2 \right)^{-1}. \quad (7)$$

The number  $N_\infty$  can be understood as an effective number of quantum states that significantly contribute to the dynamics,<sup>3</sup> or as a dynamically weighted number of phase space cells occupied by the dynamical statistical ensemble<sup>6</sup> when it has reached equilibrium. “Dynamically weighted” means that different phase space cells contribute to  $N_\infty$  with weights proportional to the probabilities of finding the system in these cells.

Although the entropic measure of phase space has a firmer theoretical foundation,<sup>8,12,20</sup> Eqs. (5)–(7) have the advantage of mathematical simplicity.

Many authors<sup>13-19</sup> have previously studied the difference between chaotic and regular quantum systems in the short- and long-time limits using the survival probability function averaged over both Hamiltonian ensembles and initial wave function conditions. Here, we use for the same purpose Heller’s function  $N(T)$ . Our aim is to determine the asymptotic law according to which  $N(T)$  approaches its final value  $N_\infty$  and to see whether this law depends on the underlying classical dynamics reflected in the statistical properties of the level spacing distributions.<sup>21-23</sup>

### II. REGULAR AND IRREGULAR DYNAMICS

The problem with Eqs. (5)–(7) is that their evaluation requires a fully resolved spectrum. However, one often wishes to extract information from a spectrum recorded at a finite resolution; large energy gaps can be measured while small intervals remain unresolved.<sup>7</sup> This is particularly the case when the spectrum exhibits a clump structure.<sup>8,15,24</sup> We assume that gross features are separated from one another and that there exists evidence that a fine structure is buried in them. Therefore, we introduce a double index notation for the quantum states, i.e., each Franck-Condon factor is denoted  $p_{Nn}$ . The first index ( $N$ ) denotes the clump while the second ( $n$ ) labels the different states concealed in it (Fig. 1). Under these circumstances, it is convenient to split the evaluation of the time-dependent terms into two contributions. Equation (6) is rewritten as follows:

$$S(T) = S_1(T) + S_2(T), \quad (8)$$

with

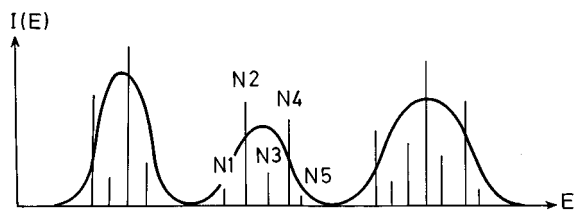


FIG. 1. Two-index notation ( $Nn$ ) for the quantum states. Index  $N$  denotes the clump, whereas the second one ( $n=1,2,3,\dots$ ) labels its fine structure.

$$S_1(T) = \sum_{N>M} \sum_{n,m} p_{Nn} p_{Mm} \{ \sin[(E_{Nn} - E_{Mm})T/2\hbar] / [(E_{Nn} - E_{Mm})T/2\hbar] \}^2, \quad (9)$$

and

$$S_2(T) = \sum_N \sum_{n>k} p_{Nn} p_{Nk} \{ \sin[(E_{Nn} - E_{Nk})T/2\hbar] / [(E_{Nn} - E_{Nk})T/2\hbar] \}^2. \quad (10)$$

The term  $S_1(T)$  denotes the contribution due to large spacings and determines the early stages of the relaxation. This term is of no interest to us because the asymptotic behavior of  $N(T)$  is determined by small frequencies, i.e., by the term  $S_2(T)$ .

In order to evaluate the second contribution  $S_2(T)$ , it is physically more reasonable to use a continuous model for the spectrum, as in a previous study.<sup>7</sup> Discrete summations in Eq. (10) are replaced by an integration over the continuous variables  $E$  and  $\omega$ . To do this, one has to know the density of states [denoted  $D(E)$ ] and that of the Franck–Condon factors [denoted  $p(E)$ ]. The spectral profile is then given by  $I(E) = p(E)D(E)$ . Also needed is the density of spacings  $D_\omega(\omega, E)$ . The important point is that the latter function exhibits a qualitatively different behavior for regular and irregular spectra. To obtain it, one first has to eliminate the so-called secular behavior of the density of states by rescaling the energies in order to get a constant average density.<sup>19,21–23</sup> Rescaled energies  $\tilde{E}$  are usually defined as

$$\tilde{E} = G(E), \quad (11)$$

where  $G(E)$  is the dimensionless integrated density of states,

$$G(E) = \int_0^E D(E) dE \quad (12)$$

equal to the total number of states between zero and  $E$ . Using these rescaled energies, one now can define rescaled frequencies  $\tilde{\omega}$  as

$$\tilde{\omega} = [G(E + \hbar\omega) - G(E)] / \hbar. \quad (13)$$

From Eqs. (12) and (13), it immediately follows that

$$d\tilde{\omega}/d\omega = D(E + \hbar\omega). \quad (14)$$

The statistical properties of these rescaled frequencies are energy independent and are known to be related to the character of the underlying classical dynamics. In the regular

case, the distribution function  $D_\omega(\tilde{\omega})$  is a constant.<sup>7,21–23</sup> The analytical formula for  $D_\omega(\tilde{\omega})$  in the case of chaotic dynamics is not known, but its qualitative behavior is quite simple.<sup>23</sup> It is equal to zero for  $\tilde{\omega}=0$ . For small values of  $\tilde{\omega}$  it is well reproduced by a Wigner distribution for nearest-neighbor spacings. It tends to a constant value for larger values of  $\tilde{\omega}$ . Then, the expression for  $S_2(T)$  writes

$$S_2(T) = \int_{-\infty}^{+\infty} dE p(E) D(E) \int_0^{w/\hbar} d\omega (d\tilde{\omega}/d\omega) \times D_\omega[\tilde{\omega}(\omega, E)] p(E + \hbar\omega) [\sin(\omega T/2) / (\omega T/2)]^2 = \int_0^{w/\hbar} g(\omega) [\sin(\omega T/2) / (\omega T/2)]^2 d\omega, \quad (15)$$

where  $w$  is some characteristic spacing smaller than the minimal width of a clump.

The function  $g(\omega)$  is defined by

$$g(\omega) = \int_{-\infty}^{+\infty} dE I(E) I(E + \hbar\omega) D_\omega[\tilde{\omega}(\omega, E)]. \quad (16)$$

In the regular case, it reduces to the spectral autocorrelation function introduced by Levine and Kinsey<sup>17</sup>

$$g(\omega) = K \int_{-\infty}^{+\infty} dE I(E) I(E + \hbar\omega), \quad (17)$$

where  $K$  (which has the dimension of an action) is the constant value of  $D_\omega(\tilde{\omega})$ .

### III. PROPERTIES OF THE FUNCTION $g(\omega)$

Since we are interested in small values of the variable  $\omega$ , it is reasonable to expand  $g(\omega)$  in a Taylor series around  $\omega=0$ . However, this cannot be done right away. In Eq. (2), the spectral profile  $I(E)$  has been defined as a Dirac comb. Hence, Eq. (17) contains the product of two distributions and does not admit a series expansion. To avoid this difficulty, the  $\delta$  functions have to be replaced by functions with a finite width (e.g., by Gaussians). This amounts to multiplying the correlation function  $C(t)$  by a damping function. These new functions [which are still related via Eq. (1)] can be substituted into Eq. (17). This gives<sup>17</sup>

$$g(\omega) = (K/\pi\hbar) \int_0^{+\infty} |C(t)|^2 \cos(\omega t) dt. \quad (18)$$

This equation is valid for the regular case only.

The following mathematical properties of  $g(\omega)$  can be derived from Eq. (18):

- $g(\omega)$  is a real, even function, whose Taylor expansion around  $\omega=0$  consists of even powers only which alternate in sign. The absence of odd terms can also be checked directly by integrating by parts under the understanding that  $I(E)$  and all of its derivatives vanish at the integration limits. For example, for the first derivative

$$g_1 \equiv dg/d\omega|_{\omega=0} = K(d/d\omega) \int_{-\infty}^{+\infty} I(E) I(E + \hbar\omega) dE|_{\omega=0}$$

$$= K\hbar \int_{-\infty}^{+\infty} I(E) I'(E) dE = 0. \quad (19)$$

Then,

$$S_2(T) = \sum_{n=0}^{\infty} (1/n!)(2/T)^{n+1} g_n \int_0^{wT/2\hbar} x^n (\sin x/x)^2 dx, \quad (20)$$

with  $n$  restricted to even integers and

$$g_n \equiv d^n g/d\omega^n|_{\omega=0}. \quad (21)$$

- (b)  $g(\omega)$  has a global maximum at  $\omega=0$ . The proof is analogous with that given by Wilkie and Brumer<sup>16</sup> in a similar study. Since  $|C(t)|^2$  is integrable and positive for all  $t$ , one has from Eq. (18),

$$(K/\pi\hbar) \int_0^{+\infty} |C(t)|^2 [1 - \cos(\omega t)] dt = g(0) - g(\omega) \geq 0. \quad (22)$$

- (c) From the Riemann–Lebesgue lemma, if the peaks are given a finite width [i.e., if  $|C(t)|^2$  is multiplied by a damping function], then

$$\lim_{\omega \rightarrow \infty} g(\omega) = 0. \quad (23)$$

- (d) The area under the curve  $g(\omega)$  is finite.<sup>17</sup> From Eq. (18),

$$\int_0^{\infty} g(\omega) d\omega = (K/\hbar) |C(0)|^2 = (K/\hbar). \quad (24)$$

In a chaotic situation, the properties of Eq. (16) are less clear and odd powers of  $\omega$  can appear in the series expansion. However, since the function  $D_{\omega}(\bar{\omega})$  vanishes for  $\bar{\omega} = 0$ , the first term  $g(0) = g_0$  vanishes from the Taylor expansion.

#### IV. THE LONG-TIME LIMIT

The integrals appearing in Eq. (20) can be calculated exactly, giving

$$S_2(T) = 2g_0 T^{-1} \{ Si(wT/\hbar) + [\cos(wT/\hbar) - 1]/(wT/\hbar) \}$$

$$+ 2g_1 T^{-2} [\ln(wT/\hbar) + \gamma - Ci(wT/\hbar)]$$

$$+ g_2 T^{-3} [(wT/\hbar) - \sin(wT/\hbar)] + (1/6)$$

$$\times g_3 T^{-4} [(wT/\hbar)^2 - 2(wT/\hbar)\sin(wT/\hbar)$$

$$+ 2 - 2\cos(wT/\hbar)] + \dots \quad (25)$$

This function admits an asymptotic expansion,

$$S_2(T) = \pi g_0 T^{-1} + 2g_1 T^{-2} \ln(wT/\hbar) + A_2 T^{-2}$$

$$+ \sum_{k=2}^{\infty} [A_{2k} T^{-2k} + B_{2k} T^{-2k} \cos(wT/\hbar)$$

$$+ C_{2k-1} T^{-2k+1} \sin(wT/\hbar)] + \dots, \quad (26)$$

with coefficients  $A_k$ ,  $B_k$ , and  $C_k$  depending on  $w$  and  $g_n$ .

The oscillatory terms in Eq. (26) have probably little physical significance. They are due to the behavior of the function  $(\sin x/x)^2$  which itself results from interference terms among the phase factors  $\exp(-iE_n t/\hbar)$  of the eigenfunctions used in the expansion of the time-dependent wave function.<sup>6</sup> Thus, they derive from a model spectrum recorded at infinite resolution, i.e., from a mathematical abstraction. If the function  $\sin^2 x/x^2$  is averaged over, i.e., if it is replaced by a Lorentzian decrease  $(1+x^2)^{-1}$ , then the oscillatory terms vanish from Eq. (26),

$$S_2(T) = \pi g_0 T^{-1} + 4g_1 T^{-2} \ln(wT/2\hbar)$$

$$+ \sum_{k=2}^{\infty} [A'_k T^{-k} + B'_k T^{-2k} \ln T], \quad (27)$$

with coefficients  $A'_k$  and  $B'_k$  depending on  $w$  and  $g_n$ .

Although Eqs. (26) and (27) are valid both for regular and irregular dynamics, a substantial difference is expected between the two cases. When the dynamics is regular, the odd coefficient ( $g_1, g_3, \dots$ ) are all equal to zero, whereas the even ones ( $g_0, g_2, \dots$ ) alternate in sign. By contrast,  $g_0$  vanishes in the chaotic case because the repulsion between energy levels precludes zero spacings.

In summary, the following simple formulae can be proposed to describe the spreading in phase space in the long-time limit. For the regular dynamics, one has

$$N(T)^{-1} = [N_{\infty}]^{-1} + 2\pi g_0 T^{-1} + C T^{-2} + O(T^{-3}). \quad (28)$$

When the dynamics is chaotic, the asymptotic behavior of  $N(T)$  has the form

$$N(T)^{-1} = [N_{\infty}]^{-1} + 4g_1 T^{-2} \ln T + C' T^{-2} + O(T^{-3}), \quad (29)$$

where  $C$  and  $C'$  are some constants depending on  $w$ , on the spectral profile, and on the function expressing the increase of the density of states as a function of energy.

#### V. DISCUSSION

If one compares regular with chaotic dynamics, it results from Eqs. (28) and (29) that  $N(T)$  approaches its final value faster in the latter case. This result, which agrees with physical intuition, is related to the phenomenon of level repulsion in chaotic spectra.<sup>21–23</sup> What is much less obvious is the presence of a logarithmic term in the asymptotic expansion (29). The agreement between Eqs. (26) and (27) gives us confidence that this term is not an artefact resulting from a constrained model: the crude averaging procedure used to derive Eq. (27) profoundly changes the higher terms of the asymptotic expansion (26) but hardly modifies the logarithmic term. The latter can be expected to reflect a fundamental property of the classical chaotic dynamics in the long-time limit.

We now wish to comment on the role played by the distribution of intensities. What has been studied here is an extrapolation formula based on existing standard models and predicting an *a priori* generic behavior. Surely, cases can be expected where the pattern of the Franck–Condon factors will correlate with that of the energy spacings to generate

exceptional (and interesting) behaviors. However, changing the spectral profile will modify the shape of the function  $g(\omega)$ , i.e., the relative magnitude of the coefficients  $g_n$  in the Taylor expansion (20), but will not modify the leading power in the asymptotic law.

Whether or not it will be easy to discern numerically a difference between Eqs. (28) and (29) is a question which remains to be studied. It may well turn out (and there are even reasons to believe) that the difference will be conspicuous only at the very end of the relaxation, i.e., when most of the available phase space has been sampled.

The long-time behavior predicted by Eqs. (28) and (29) differs from the  $T^{-2}$  asymptotic dependence predicted by Eqs. (5) and (6) for systems with a finite number of states. This is hardly surprising. Replacing a discrete summation by an integration over a continuum of states is known to change the law of evolution, as in the derivation of the Golden Rule where this procedure changes the time dependence of the transition probability from a quadratic to a linear law.<sup>25</sup>

## ACKNOWLEDGMENTS

V.B.P.-V. is grateful to the Fonds National de la Recherche Scientifique (Belgium) and to the Université de Liège for a travel grant that made possible his stay abroad. J.C.L. wishes to thank Professor J. P. Gaspard for a useful discussion. He is indebted to the Fonds de la Recherche Fondamentale Collective for a research grant (No. 94-03-08960).

<sup>1</sup>E. J. Heller, *J. Chem. Phys.* **68**, 2066, 3891 (1978); *Acc. Chem. Res.* **14**, 368 (1981).

<sup>2</sup>D. Imre, J. L. Kinsey, A. Sinha, and J. Krenos, *J. Phys. Chem.* **88**, 3956 (1984).

<sup>3</sup>E. J. Heller, *Phys. Rev. A* **35**, 1360 (1987).

<sup>4</sup>B. R. Johnson and J. L. Kinsey, *J. Chem. Phys.* **91**, 7638 (1989).

<sup>5</sup>R. Schinke and V. Engel, *J. Chem. Phys.* **93**, 3252 (1990).

<sup>6</sup>J. C. Lorquet and V. B. Pavlov-Verevkin, *J. Chem. Phys.* **93**, 520 (1990).

<sup>7</sup>J. C. Lorquet, Y. M. Engel, and R. D. Levine, *Chem. Phys. Lett.* **175**, 461 (1990).

<sup>8</sup>F. Remacle and R. D. Levine, *Chem. Phys. Lett.* **181**, 307 (1991); *J. Chem. Phys.* **98**, 2144 (1993); in *Dynamics of Molecules and Chemical Reactions*, edited by Robert E. Wyatt and John Z. H. Zhang (Marcel Dekker, New York, 1996), p. 1.

<sup>9</sup>D. Chapman, J. M. Bowman, and B. Gazdy, *J. Chem. Phys.* **96**, 1919 (1992).

<sup>10</sup>R. E. Wyatt and C. Iung, *J. Chem. Phys.* **98**, 5191 (1993).

<sup>11</sup>K. Hirai, E. J. Heller, and P. Gaspard, *J. Chem. Phys.* **103**, 5970 (1995).

<sup>12</sup>V. B. Pavlov-Verevkin and J. C. Lorquet, *J. Chem. Phys.* **104**, 1362 (1996).

<sup>13</sup>P. Pechukas, *Chem. Phys. Lett.* **86**, 553 (1982).

<sup>14</sup>L. Leviandier, M. Lombardi, R. Jost, and J. P. Pique, *Phys. Rev. Lett.* **56**, 2449 (1986).

<sup>15</sup>J. P. Pique, Y. Chen, R. W. Field, and J. L. Kinsey, *Phys. Rev. Lett.* **58**, 475 (1987).

<sup>16</sup>J. Wilkie and P. Brumer, *Phys. Rev. Lett.* **67**, 1185 (1991).

<sup>17</sup>R. D. Levine and J. L. Kinsey, *Proc. Natl. Acad. Sci. USA* **88**, 11 133 (1991).

<sup>18</sup>Y. Alhassid and R. D. Levine, *Phys. Rev. A* **46**, 4650 (1992); Y. Alhassid and N. Whelan, *Phys. Rev. Lett.* **70**, 572 (1993).

<sup>19</sup>S. Mahapatra, R. Ramaswamy, and N. Sathyamurthy, *J. Chem. Phys.* **104**, 3989 (1996).

<sup>20</sup>F. Iachello and R. D. Levine, *Europhys. Lett.* **4**, 389 (1987); R. D. Levine, *Adv. Chem. Phys.* **70**, 53 (1988).

<sup>21</sup>N. Rosenzweig and C. E. Porter, *Phys. Rev.* **120**, 1698 (1960).

<sup>22</sup>E. Haller, H. Köppel, and L. S. Cederbaum, *Chem. Phys. Lett.* **101**, 215 (1983); Th. Zimmermann, L. S. Cederbaum, H. D. Meyer, and H. Köppel, *J. Phys. Chem.* **91**, 4446 (1987); Th. Zimmermann, L. S. Cederbaum, and H. Köppel, *Ber. Bunsenges. Phys. Chem.* **92**, 217 (1988).

<sup>23</sup>C. E. Porter, in *Statistical Theories of Spectra: Fluctuations*, edited by C. E. Porter (Academic, New York, 1965), p. 511.

<sup>24</sup>C. E. Hamilton, J. L. Kinsey, and R. W. Field, *Annu. Rev. Phys. Chem.* **37**, 493 (1986).

<sup>25</sup>E. M. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970), p. 479.