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# Intramolecular vibrational relaxation seen as expansion in phase space. II. Reference ergodic systems

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The aim of the paper is to estimate the volume of phase space that is, in principle, available to a nonstationary wave packet during its intramolecular vibrational relaxation. For that purpose, use is made of the maximum entropy method, together with the concept of constrained ergodicity to construct two so-called reference ergodic systems. The first one concerns thermal excitation processes. In that case, the only two constraints that are imposed on the intramolecular dynamics arise from the normalization of the wave function and from the conservation of energy. These constraints affect the zeroth and first moments of the spectrum. The second reference system concerns a situation where, as an additional constraint, use is made of the information that the system has been prepared spectroscopically, i.e., by a specific excitation process, consisting in the coherent excitation of an initial pure state. Then, the second moment of the spectrum, denoted $\sigma$, is shown to provide the appropriate additional constraint. Translated into the time domain, the prior knowledge of the dynamics used as a constraint is limited to an infinitesimally brief period of time $[0,dt]$ with the remaining evolution determined by the maximum entropy method. The spectroscopic reference system constructed in that way can be understood as the one that samples the maximal volume of phase space available to a wave packet having a specified average energy and being put in motion by a specified initial force. Closed-form expressions are obtained for the phase space volumes occupied by these two reference systems for various simple parametrizations of the function $D(E)$ that expresses the density of states as a function of the internal energy (power laws or exponential increase). Thermal reference systems are found to sample a larger volume of phase space than their spectroscopic counterparts. The difference between these two cases depends critically on the value of $\sigma$, and also on the symmetry characteristics of the excitation process. In general, the volumes occupied by the reference systems, thermal as well as spectroscopic, can be expressed as $\eta E_{\mathrm{av}} D(E_{\mathrm{av}})$, where $E_{\mathrm{av}}$ is the (conserved) average energy of the wave packet and $\eta$ is a correcting factor that depends on the functional form of $D(E)$ and on the nature of the imposed constraints. In all cases studied, the value of $\eta$ was found not to greatly differ from 1. The method has been applied to the analysis of three experimental photoelectron spectra presenting different spectral characteristics ($\tilde{X}\ ^2A_1$ state of $\mathrm{NH}_3^+$, $\tilde{X}\ ^2B_3$ state of $\mathrm{C}_2\mathrm{H}_4^+$, and the $\tilde{X}\ ^2A''$ state of $\mathrm{C}_2\mathrm{H}_3\mathrm{F}^+$). The fractional occupancy index $F$ defined by Heller as the fraction of the available phase space eventually explored up to the break time $T_B$ could be determined. After a time of the order of 100 fs, $F$ was found to be of the order of a few percent for thermal excitation. When the molecule presents some symmetry, the expansion of the wave packet is restricted to that part of phase space spanned by the totally symmetric wave functions. The use of this additional a priori knowledge increases the fractional index $F$. [S0021-9606(96)02804-9]

## I. INTRODUCTION

The efficiency of the intramolecular vibrational energy relaxation which follows the initial excitation of an isolated molecule by photon absorption is of central interest in the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular decay.[1,2] In this connection, an especially appealing concept has been introduced by Heller,[3,4] namely the fraction $F$ of the available phase space eventually explored. The aim of the present paper is to specify the meaning of the word *available* and to propose a simple way to estimate $F$. For that purpose, two interesting tools have been developed.

First, a precious source of information on flows in phase space following an initial excitation derives from the connection between intramolecular dynamics and spectroscopy.[3–9] Autocorrelation functions, obtained as the Fourier transform of the vibrational structure of an electronic transition, have provided much insight.[9–22] Denoting the energies and Franck–Condon factors of a spectrum by $E_k$ and $p_k$, respectively, the autocorrelation function is equal to

$$C(t)=\sum_k p_k \exp(-iE_k t/\hbar). \tag{1.1}$$

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The analysis of the problem requires a proper definition of a measure of volumes in phase space. For an excitation process obeying the Franck–Condon principle, Stechel and Heller[3,23–25] measure these volumes by the quantity

$$N^{\infty}=\left(\sum_{k} p_{k}^{2}\right)^{-1}. \tag{1.2}$$

In fact, the number $N^{\infty}$ measures a dynamically weighted number of phase space cells occupied by a dynamical statistical ensemble when it has reached equilibrium.[17] "Dynamically weighted" means here that different phase space cells contribute to $N^{\infty}$ with a weight proportional to the probability of finding the system in each cell.

The second essential conceptual tool derives from the maximum entropy method,[26–34] which helps us to estimate both the numerator and the denominator of the fraction $F$, defined as[3,4]

$$F=N^{\infty}/N^{*}. \tag{1.3}$$

For the numerator, it has been pointed out by Levine and his associates that entropy provides an adequate measure for volumes in phase space.[29,30] Equation (1.2) can be replaced by

$$N^{\infty}=\exp(-\Sigma p_{k} \ln p_{k}). \tag{1.4}$$

The denominator $N^{*}$ measures the number of available phase space cells, i.e., the volume which could have been accessed in a hypothetical situation, defined as as ergodic as possible when the *appropriate* constraints are taken into account. The knowledge of the number $F$ serves to determine whether the system in fact accesses a region of phase space more limited than what we think it should have, i.e., if only the *essential, a priori* known constraints had been retained. The maximum entropy method provides the adequate background to clarify these specifications. Heller[3] invoked the concept of "ergodicity under prior constraints" which is clearly in the spirit of this method even when a different measure is adopted. He recognized that, if enough constraints are introduced, then the system becomes trivially ergodic[35] and proposed to retain the spectral envelope (equivalent to a knowledge of the dynamics during a very short time) as the only constraint.

What we want to do is, for specific molecules, to compare a number $N^{\infty}$ of experimental origin (i.e., measuring the asymptotic propagation in phase space of an actual wave packet after a time limited by practical reasons[10] to about 200 femtoseconds) with some convenient yardsticks (hereafter denoted "reference ergodic systems") in order to evaluate the relative amount of phase space that has been actually sampled. We wish to identify the nature and the importance of the different constraints imposed on the intramolecular dynamics. Two natural standards of comparison can be proposed off hand.

(i) The volume of phase space that would have been sampled in the absence of any constraint other than the conservation of energy. This corresponds to a nonspecific (e.g., thermal) preparation of the system of reference. The obtained quantity $N^{*}$ will be affixed by a single asterisk, to indicate nonspecific excitation.

(ii) The volume of phase space that would have been sampled if, as an additional constraint, use is made of the information that the system has been prepared spectroscopically, i.e., by a specific excitation process, consisting in the coherent excitation of an initial pure state. The resulting quantity $N^{**}$ is then affixed with two asterisks.

In every case, both $N^{*}$ and $N^{**}$ will be calculated by maximizing the entropy under the constraint of energy conservation, which is of crucial importance in our problem.

## II. REFERENCE ERGODIC SYSTEMS

A reference ergodic system is defined as the most ergodic equilibrium state possible under particular constraints imposed on the system. Therefore, it should fulfill the following requirements.

A reference ergodic system should be characterized by a maximal value of an appropriate measure under constraints imposed by the equations of motion and by a particular preparation (thermal or spectroscopic).

Whatever the preparation of the system, an obviously essential restriction is that the reference ergodic systems should be be characterized by the same value of the internal energy as the actual system under study.

Reference ergodic systems describe an equilibrium situation. Hence, they are represented by a diagonal density operator

$$\rho=\sum_{k} p_{k}|k\rangle\langle k|, \tag{2.1}$$

where $|k\rangle$ are the eigenfunctions of the Hamiltonian $H$ of the system.

Next, we recognize the importance of specifying the number and nature of the relevant degrees of freedom. In the sequential model developed by Remacle and Levine,[21,22] the sampling of phase space proceeds stepwise: during each time regime, it is limited to a single region of phase space. An additional region is accessed during the next period of time.[36–38] This stepwise process is associated with a progressive reduction of the number of good quantum numbers. It is accompanied by a progressive splitting of the spectral lines, and by a progressive increase of the density of resolved states. It is then essential to specify where the reference system is located within the hierarchy of Hamiltonians[22] in order to limit the splittings which are taken into account in the "fully resolved spectrum." For our present purposes, a natural choice of the model Hamiltonian is as follows.

The density of states $D(E)$ of the reference ergodic system should be generated by an appropriate selection of those degrees of freedom that are recognized as being relevant to the problem at hand. Since our aim is to obtain information on intramolecular vibrational energy relaxation within a lifetime of chemical interest, we consider only the set of $3N-6$ vibrational degrees of freedom (including the internal rotations). External rotations are disregarded since the information leading to the number $N^{\infty}$ is ideally extracted from spectra of jet-cooled molecules and since the correlation function to be analyzed has been freed from the overall rotation.[10] Electronic and nuclear spins are also absent from the model, as well as splittings resulting from tunneling between isomers if the inversion barrier separating them is so high that tunneling is slow with respect to a timescale of chemical interest.

The quantities of interest are expressed as traces, which can be evaluated either as discrete summations (if the states $|k\rangle$ form a sparse set), or as integrals involving a density of states $D(E)$ that steeply increases with energy (if the number of degrees of freedom to be taken into account is large). The former procedure is always possible since exact state-counting algorithms are available.[1,2,39] However, the use of a continuous approximation offers definite advantages, because it leads to compact closed-form expressions given later. The needed quantities are

$$\sum_k p_k = \int_0^{\infty} p(E)D(E)dE \equiv \int_0^{\infty} I(E)dE = 1. \tag{2.2}$$

[For optical processes, $p(E)$ is the distribution function of the Franck–Condon factors, while $I(E) \equiv p(E)\ D(E)$ is the spectral profile.] Equation (2.2) expresses the normalization condition of these quantities. The moments of the spectrum are given by

$$\sum_k p_k E_k^n = \int_0^{\infty} E^n I(E)dE \equiv \langle E^n \rangle. \tag{2.3}$$

The measure defined in Eq. (1.2) then becomes

$$\sum_k p_k^2 = \int_0^{\infty} I(E)^2/D(E)dE. \tag{2.4}$$

Finally, the entropy of the reference ergodic system is defined as

$$S = -\sum_k p_k \ln p_k = -\int_0^{\infty} dE I(E) \ln[I(E)/D(E)]. \tag{2.5}$$

These integrals can exist only if $I(E)$ tends to zero as $E$ goes to infinity. This implies that the distribution function $p(E)$ has to cancel the steep increase with energy of the density of states $D(E)$. This is automatically taken care of in the maximum entropy method if the constraints are the first few moments of the distribution. We therefore adopt the formalism implemented by Levine and Bernstein.[28,31–34] The Lagrangian functional to be varied with respect to $p(E)$ writes

$$L = -\int_0^{\infty} dE\ D(E)\Bigg( p(E)\ln[p(E)] + (\lambda_0 - 1)p(E) + \sum_{r=1} \lambda_r E^r p(E)\Bigg), \tag{2.6}$$

where the quantities $(\lambda_0 - 1)$ and $\lambda_r$ are Lagrange multipliers. Minimizing this functional, one finds

$$I(E) = D(E)\prod_{r=0} \exp(-\lambda_r E^r). \tag{2.7}$$

Even a single constraint limited to the first moment of the distribution ensures convergence since the density of states of a set of oscillators increases less rapidly than an exponential decreases. On the other hand, the situation is quite different with the measure adopted by Stechel and Heller. If one tries to minimize the functional (2.4) with constraints given by Eq. (2.3), one easily arrives at the solution

$$I(E) = D(E)\sum_{r=0} \lambda_r E^r. \tag{2.8}$$

One sees that it is impossible to cancel the rapid increase of $D(E)$ with energy unless an infinite number of moments are introduced as constraints. Heller[3,6] overcame this difficulty by adopting as a single constraint the envelope corresponding to very short-time dynamics, which is equivalent to fixing the values of a large number of moments. However, the overall evidence is clearly in favor of Eq. (2.7). In the present work, we use it to determine the model envelope of the reference ergodic system by the maximum entropy method.

## III. THERMAL REFERENCE SYSTEMS

In the absence of any particular information, only two *a priori* restrictions should be applied to any conservative intramolecular process, because they derive from the equations of motion: the normalization condition and the law of conservation of energy. Then, the maximum entropy continuous distribution function $p(E)$ should, from Eq. (2.7), be expressed in terms of just two Lagrange multipliers, i.e., should be represented by the function

$$p(E) = \exp(-\lambda_0)\exp(-\lambda_1 E). \tag{3.1}$$

The Lagrange multipliers are determined from the constraints

$$\mathrm{Tr}(\rho) = \int_0^{\infty} I(E)dE = \exp(-\lambda_0)\int_0^{\infty} \exp(-\lambda_1 E)\ D(E)dE = 1 \tag{3.2}$$

and

$$\mathrm{Tr}(H\rho) = \int_0^{\infty} I(E)EdE = \exp(-\lambda_0)\int_0^{\infty} \exp(-\lambda_1 E)ED(E)dE = E_{\mathrm{av}}. \tag{3.3}$$

The entropy is then equal to[28,31–34]

$$S^* = -\int_0^{\infty} dEp(E)D(E)\ln[p(E)] = \lambda_0 + \lambda_1 E_{\mathrm{av}} \tag{3.4}$$

and the entropic measure of the reference system is given by

$$N^* = \exp(S^*) = \exp(\lambda_0)\exp(\lambda_1 E_{\mathrm{av}}). \tag{3.5}$$

Hence, from Eqs. (3.2) and (3.3),

$$\exp(\lambda_0) = \int_0^\infty \exp(-\lambda_1 E) D(E)\, dE \equiv Z, \tag{3.6}$$

$$E_{\text{av}} = -\partial(\ln Z)/\partial\lambda_1. \tag{3.7}$$

The reference system constructed by limiting the constraints to Eqs. (3.2) and (3.3) is seen to be the well-known canonical ensemble.[28,31–34] The rôle played by the two Lagrange parameters is clear: the partition function $Z$ is equal to $\exp(\lambda_0)$ and the Lagrange parameter $\lambda_1$ represents an inverse temperature.[34] In statistical physics,[40] these ensembles have long been known to describe the most probable state of a system in thermal equilibrium with a prescribed average energy. Thus, the reference ergodic system predicted by the maximum entropy formalism constructed with just two constraints confirms physical intuition and will therefore be referred to as thermal.

Closed form solutions are easily obtained if the density of states $D(E)$ is fitted to simple algebraic expressions. Three approximations can be proposed. Remarkably enough, they lead to results having the same order of magnitude.

If $D(E)$ increases exponentially with the energy, i.e., if

$$D(E) = B \exp(\beta E) \tag{3.8}$$

it follows from Eqs. (3.2)–(3.5) that the entropic measure is given by

$$N^* = eE_{\text{av}} D(E_{\text{av}}). \tag{3.9}$$

If, on the other hand, the density of states increases as some power of $E$, i.e., if

$$D(E) = CE^{s-1}, \tag{3.10}$$

where $C$ and $s$ are empirical parameters, then it is easily found that

$$N^* = (s-1)!(e/s)^s E_{\text{av}} D(E_{\text{av}}) \equiv \eta^*(s) E_{\text{av}} D(E_{\text{av}}). \tag{3.11}$$

For not too small values of $s$, one has

$$N^* \approx (2\pi/s)^{1/2} E_{\text{av}} D(E_{\text{av}}). \tag{3.12}$$

For concrete applications, the parameter $s$ is expected to range between about 3 and, say, 10. Within these limits, the function $(s-1)!(e/s)^s$ slowly varies between 1.49 and 0.8. The correcting factor $\eta^*(s)$ is, in this case, always close to unity.

A popular and accurate parametrization of the density of states is provided by the Whitten–Rabinovitch approximation[1,2]

$$D(E) = C(E+\omega)^{s-1}, \tag{3.13}$$

where parameter $\omega$ is of the order of the zero-point energy. Substituting Eqs. (3.1) and (3.13) into Eq. (3.2) and expanding the power by the binomial formula, one gets

$$Z = \exp(\lambda_0) = C(s-1)!\lambda_1^{-s} \exp(\lambda_1 \omega) \tag{3.14}$$

provided that

$$(\omega\lambda_1)^s/s! \ll 1. \tag{3.15}$$

Substitution into Eq. (3.7) leads to

$$\lambda_1 = s/(E_{\text{av}} + \omega) \tag{3.16}$$

confirming the fact that the quantity $\lambda_1^{-1}$ has to be interpreted as the average energy per oscillator, in conformity with the equipartition theorem of classical mechanics. Substituting Eqs. (3.13), (3.14), and (3.16) into Eq. (3.5) gives

$$N^* = (s-1)!(e/s)^s (1+\omega/E_{\text{av}}) E_{\text{av}} D(E_{\text{av}}), \tag{3.17}$$

$$N^* \approx (2\pi/s)^{1/2} (1+\omega/E_{\text{av}}) E_{\text{av}} D(E_{\text{av}}) \tag{3.18}$$

with Stirling's approximation.

The condition of validity of these equations is obtained by substituting Eq. (3.16) into Eq. (3.15):

$$[\omega/(E_{\text{av}}+\omega)]^s \ll (2\pi s)^{1/2} e^{-s}. \tag{3.19}$$

When conditions (3.15) and (3.19) are fulfilled, i.e., when Eq. (3.17) is valid, the factor $(1+\omega/E_{\text{av}})$ is not far above 1. On the other hand, for molecules larger than tetra-atomics, the factor $(2\pi/s)^{1/2}$ in Eq. (3.18) is smaller than 1, because in the Whitten–Rabinovitch approximation,[1,2] the parameter $s$ represents the effective number of oscillators and is usually larger than the empirical exponent defined in Eq. (3.11). The final conclusion is again that $N^*$ has the same order of magnitude as the product $E_{\text{av}} D(E_{\text{av}})$.

In summary, for thermal reference systems, an order of magnitude of $N^*$ can in practice be obtained by the very simple equation

$$N^* = \eta^* E_{\text{av}} D(E_{\text{av}}) \approx E_{\text{av}} D(E_{\text{av}}) \tag{3.20}$$

with $\eta^*$ defined as a correcting function which, usually, is close to 1.

## IV. SPECTROSCOPIC REFERENCE SYSTEMS

Can one arrive at as simple results for a spectroscopic preparation? It is well known in the maximum entropy formalism[28,31–34] that the number and nature of the constraints depend on the preparation of the system. If the latter results from an electronic transition in a polyatomic molecule, the initial state is represented by a multidimensional, approximately Gaussian wave packet in a nonstationary situation.[5–9] The localized nature of the initial wave packet in configuration and phase spaces leads to a set of Franck–Condon factors having a characteristic hump followed by a rapid decrease in the high energy region, associated with localization in the energy domain.

Therefore, compared with the thermal systems studied in Sec. III, an additional constraint has to be added to the two necessary requirements expressed in Eqs. (3.2) and (3.3) to specify the spectroscopic origin of the initial state. In physical terms, the additional information concerns the existence of a strongly localized Franck–Condon region. The most natural way to translate this in the maximum entropy formalism is to impose a restriction bearing on the second moment of the spectrum since the latter quantity determines the width of the Franck–Condon region in the energy representation.

$$\int_0^\infty I(E)E^2dE=\langle E^2\rangle\equiv\sigma. \tag{4.1}$$

Thus, the second moment of the spectral distribution, henceforth denoted $\sigma$, is smaller than that of thermal reference systems because it is restricted by the localized nature of the initially prepared state.

The maximum entropy distribution $p(E)$ associated with a spectroscopic preparation writes, as a result of Eq. (2.7):

$$p(E)=\exp(-\lambda_0)\exp(-\lambda_1 E)\exp(-\lambda_2 E^2). \tag{4.2}$$

As explained by Levine and Kinsey,[33] "even when the magnitude of the average values is not given, the mere identification of the observables that serve as constraints suffices to determine the functional form of the distribution." The value of the third Lagrange multiplier $\lambda_2$ is then determined by maximizing the entropy with Eq. (4.1) used as the third constraint. One is then looking for a maximum entropy reference system with a specified width of the Franck–Condon region. That this choice very naturally specifies the spectroscopic origin of the ergodic reference system receives further substantiation from the following considerations.

In order to determine the additional constraint characteristic of a spectroscopic preparation, it is advantageous to consider the time-dependent formulation of electronic spectroscopy.[5–9] Heller based his definition of the stochasticity of a spectroscopic system on "the division of dynamical information into that which is known initially, and that which remains to be discovered."[6] He developed the concept of a spectral envelope implying knowledge of the dynamics during a restricted period of time $[0,T^*]$. He noticed that there is some freedom of choice as to the value to be given to time $T^*$ and proposed to adopt for it the time at which the square modulus of the autocorrelation function admits its first minimum, at the end of its initial decay and before its first recurrence.

We suggest the following alternative. Since $C(t)$ is a complex function, the minimal information on it involves two independent equations: one for its real and one for its imaginary part. A well-known theorem on Fourier transforms relates the values of its derivatives at time $t=0$ to the moments of the spectrum. From Eq. (1.1), one gets easily

$$dC/dt|_{t=0}=-(i/\hbar)\sum_k p_kE_k=-(i/\hbar)E_{\mathrm{av}}, \tag{4.3}$$

$$d^2C/dt^2|_{t=0}=-(1/\hbar)^2\sum_k p_kE_k^2=-(1/\hbar)^2\sigma. \tag{4.4}$$

Furthermore,

$$d^2|C(t)|^2/dt^2|_{t=0}=-(2/\hbar)^2\sum_k p_k(E_k-E_{\mathrm{av}})^2$$
$$=-(2/\hbar)^2(\sigma-E_{\mathrm{av}}^2). \tag{4.5}$$

These derivatives are related to the dephasing time $\tau_D$ of the wave packet, which, as shown by Bixon and Jortner,[41] represents in classical terms the time needed for it to move a distance equal to its width when sliding along a potential energy curve having a negative slope equal to $F$:

$$(h/2\pi\mu\nu)^{1/2}=(F/2m)\hbar^2/(\sigma-E_{\mathrm{av}}^2). \tag{4.6}$$

The second derivative of the correlation function at $t=0$ is thus determined by the slope of the potential energy surface in the Franck–Condon region. Therefore, imposing $E_{\mathrm{av}}$ and $\sigma$ as constraints in Eq. (4.2) amounts to determining the largest volume of phase space sampled by a wave packet having a specified average energy and being put in motion by a specified initial force.

In conclusion, we submit that the present procedure to construct the spectroscopic reference ergodic system combines the main ideas developed by Heller[3,6] and those included in the maximum entropy method. The spectroscopic reference system should be determined by a minimal set of constraints. In Heller's method, the (short) period of time $[0,T^*]$ during which the dynamics is assumed to be known is used to determine the constraints. By dealing separately with the real and imaginary parts of the autocorrelation function, one is able to squeeze this period of time down to the infinitesimally short interval $[0,dT]$. (Recall that since the real part of the correlation function is an even function of time, its second derivative can be calculated with just a single finite element.) What remains to be discovered after time $dT$ is determined by the maximum entropy method. Adding the third and fourth moments of the spectrum as additional constraints would amount to assuming prior knowledge of the dynamics during a larger period of time equal to $[0,2dT]$. Let us now evaluate $N^{**}$ in different approximations.

### A. Power law for the density of states

If the density of states is fitted to Eq. (3.10), with Franck–Condon factors given by Eq. (4.2), then the expressions for the first three spectral moments are

$$Ce^{-\lambda_0}(2\lambda_2)^{-s/2}\Gamma(s)\exp(z^2/4)D_{-s}(z)=1, \tag{4.7}$$

$$Ce^{-\lambda_0}(2\lambda_2)^{-(s+1)/2}\Gamma(s+1)\exp(z^2/4)D_{-(s+1)}(z)=E_{\mathrm{av}}, \tag{4.8}$$

$$Ce^{-\lambda_0}(2\lambda_2)^{-(s+2)/2}\Gamma(s+2)\exp(z^2/4)D_{-(s+2)}(z)$$
$$=\langle E^2\rangle\equiv\sigma, \tag{4.9}$$

where

$$z=\lambda_1(2\lambda_2)^{-1/2} \tag{4.10}$$

and $D_{-s}(z)$ is the parabolic cylinder function[42] characterized by the following recurrence relation:

$$D_{-(s+2)}(z)=[D_{-s}(z)-zD_{-(s+1)}(z)]/(s+1). \tag{4.11}$$

Introducing a shorthand notation,

$$\mu_s(z)\equiv D_{-(s+1)}(z)/D_{-s}(z) \tag{4.12}$$

it turns out that all important quantities can be expressed as a function of the variable $z$:

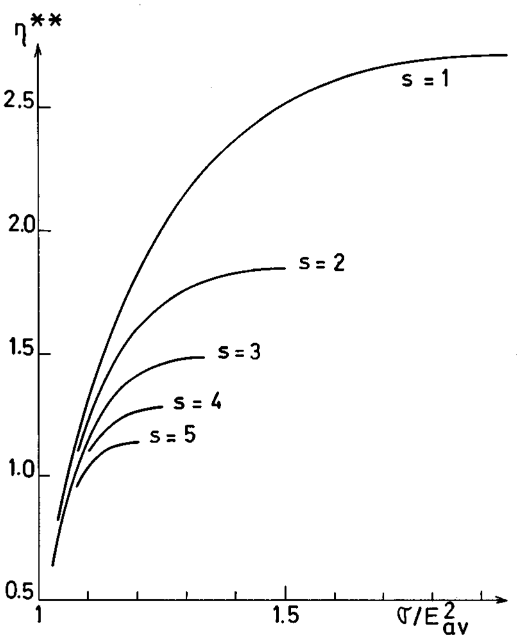

FIG. 1. Value of the correcting factor $\eta^{**}$ for a spectroscopic transition as a function of the dimensionless parameter $\sigma/E^2_{\mathrm{av}}$ for various parametrizations of the density of states.

$$S^{**}=\lambda_0+\lambda_1 E_{\mathrm{av}}+\lambda_2\sigma$$
$$=S_0+z^2/4+0.5sz\mu_s(z)+\ln[D_{-s}(z)]-s\ \ln[\mu_s(z)], \tag{4.13}$$

where

$$S_0\equiv\ln[C\Gamma(s)(E_{\mathrm{av}}\sqrt{e}/s)^s] \tag{4.14}$$

contains all the terms which do not depend on $z$. This leads to an expression for $N^{**}$ having the same form as Eq. (3.20):

$$N^{**}=\eta^{**}(z)E_{\mathrm{av}}D(E_{\mathrm{av}}), \tag{4.15}$$

where

$$\eta^{**}(z)=\{\sqrt{e}/[s\mu_s(z)]\}^s\Gamma(s)D_{-s}(z)$$
$$\times\exp[z^2/4+0.5sz\mu_s(z)]. \tag{4.16}$$

The reduced variable $z$ can be replaced by another dimensionless parameter $\sigma/E^2_{\mathrm{av}}$ since

$$\sigma/E^2_{\mathrm{av}}=[1-z\mu_s(z)]/[s\mu_s(z)^2]. \tag{4.17}$$

In summary, for spectroscopic systems, one again arrives at

$$N^{**}=\eta^{**}E_{\mathrm{av}}D(E_{\mathrm{av}}), \tag{4.18}$$

where the correcting factor $\eta^{**}$ is related to the shape of the spectral envelope via a single parameter $\sigma/E^2_{\mathrm{av}}$. A graph showing this relationship is given in Fig. 1. Analytical expressions and tables of numerical values can be obtained from the authors.

### B. Exponentially increasing density of states

The study of spectroscopic reference systems when the density of states can be parametrized by Eq. (3.8) proceeds in a completely analogous way. The previous equations, (4.7)–(4.15) are easily adapted to the present case, simply by putting $s=1$, replacing $C$ by $B$, and $\lambda_1$ by $\lambda_1-\beta$. Furthermore, Eq. (4.14) must be replaced by

$$S_0=0.5+\beta E_{\mathrm{av}}+\ln(BE_{\mathrm{av}}). \tag{4.19}$$

## V. DISCUSSION

As shown by Eqs. (3.20) and (4.18), the maximum entropy method leads to expressions for the measure of thermal and spectroscopic reference systems which all have the same general form. Whatever the parametrization adopted for the density of states, $N^*$ and $N^{**}$ increase with energy as the product $E_{\mathrm{av}}D(E_{\mathrm{av}})$. Both for thermal and spectroscopic systems, the correcting factor $\eta$ can, in principle, vary between 0 and $e$. In practice, however, $\eta^*$ and $\eta^{**}$ are never very different from one. Therefore, as a first approximation, an order of magnitude of both $N^*$ and $N^{**}$ is given by the product $E_{\mathrm{av}}D(E_{\mathrm{av}})$.

The two-parameter functions, Eqs. (3.8) and (3.10), which have been used to fit the density of states function $D(E)$ are not very flexible, but they generate results that are as simple as possible. The use of a three-parameter empirical equation, as the Whitten–Rabinovitch approximation, is possible for thermal excitation but is much more difficult for spectroscopic processes, because the results would then no longer depend on a single reduced variable.

As expected, thermal reference systems are found to sample a larger volume of phase space than their spectroscopic counterparts. For a given value of the average energy $E_{\mathrm{av}}$, the broader the width of the Franck–Condon region, the larger the initial force acting on the wave packet [according to Eq. (4.6)], and the larger the volume of the *a priori* available phase space, i.e., the closer $\eta^{**}$ and $\eta^*$. The second moment $\sigma$ is thus an informative observable.

However, an important distinction has to be introduced in the comparison between thermal and spectroscopic reference systems. When the molecule under study presents some symmetry, the expansion of the initial wave packet in the basis of the eigenfunctions of the final state is restricted by selection rules to the subset of eigenstates belonging to the totally symmetric representation. This implies that the function $D(E)$ that appears in Eq. (4.18) is to be understood as the density of those states only. In other words, the number $N^{**}$ estimated from a state counting procedure carried out, e.g., by the Beyer–Swinehardt algorithm[2,39] has to be corrected. At sufficiently high energies, the partial density of states $D^{\Gamma i}$ corresponding to a particular representation $\Gamma_i$ is proportional to the square of its dimension $[\Gamma_i]$,[43–46] i.e.,

$$D^{\Gamma 1}/D^{\Gamma 2}=[\Gamma_1]^2/[\Gamma_2]^2. \tag{5.1}$$

A thermal process, on the other hand, is not subject to symmetry restrictions.

TABLE I. Analysis of the sampling of phase space by the break time $T_B$ from three experimental photoelectron spectra.

| | $NH_3^+$ ($\tilde{X}\ ^2A_1$) | $C_2H_4^+$ ($\tilde{X}\ ^2B_3$) | $C_2H_3F^+$ ($\tilde{X}\ ^2A''$) |
|---|---|---|---|
| $E_{av}$ (cm$^{-1}$) | 6300 | 1500 | 2750 |
| $\sqrt{\sigma}$ (cm$^{-1}$) | 7000 | 2140 | 3460 |
| $T_B$ (fs) | 34 | 160 | 120 |
| $N^\infty$ | 12 | 13 | 22 |
| $E_{av}\ D(E_{av})$ | 220 | 60 | 610 |
| $F^*$ | 0.03 | 0.1 | 0.025 |
| $F^{**}$ | 0.17 | 0.25 | 0.05 |

## VI. ANALYSIS OF EXPERIMENTAL RESULTS

The previous formulas will now be applied to an analysis of actual experimental photoelectron spectra. In order to examine various possibilities, three different cases will be considered. First, a spectrum consisting in a very long progression of a single frequency. Second, a spectrum involving three progressions with the most intense transition leading to the vibrationless level of the upper state. The third spectrum consists again of a superposition of three progressions, but with a less regular distribution of the intensities.

In all of the three cases, the autocorrelation function could be determined at least up to Heller's break time[3] $T_B$, equal to

$$T_B = h/\delta, \tag{6.1}$$

where $\delta$ is the smallest energy gap between two optically active vibrational levels (i.e., having nonzero Franck–Condon factors in the spectrum).[17] The break time $T_B$ provides a convenient reference, because it determines the end of the first step of phase space sampling, which consists in a rapid energy exchange among the subset of optically active, totally symmetric normal modes, i.e., in a process where the dephasing of the wave packet is governed by large splittings. The rate of exploration of phase space then drops down to a very small value by that time,[3,17] but only temporarily.[22,36–38] Reported here are the number $N^\infty$ and the fractions $F^*$ and $F^{**}$ of phase-space cells sampled by time $T_B$. An overview of the results is presented in Table I.

### A. The $\tilde{X}\ ^2A_1$ state of $NH_3^+$

The first band of the photoelectron spectrum of $NH_3$ leading to the ground electronic state of the $NH_3^+$ ion ($\tilde{X}\ ^2A_1$) exhibits a rich vibrational structure,[47] but limited to a single progression involving a single frequency. The excited vibrational normal mode is the $a_1$ bending mode $\nu_2$ which produces the inversion of ammonia. Sixteen vibrational levels (from $v=0$ to $v=15$) are detected in the progression. This indicates a large amplitude vibrational motion of the wave packet, but along a single degree of freedom only. Values for the vibrational frequencies of the $NH_3^+$ ion have been reported[48] and can be used to calculate the density of states. The function $D(E)$ can be fitted either to an exponential $[D(E) \approx 0.0056 \exp(3.1\times10^{-4}E)$, with $E$ in wave number units], or to a power law $[D(E) \approx 1.48\times10^{-13}E^3]$, or to a Whitten–Rabinovitch expression $[D(E) \approx 6.7\times10^{-18}(E+2000)^4]$.

Averaging over these results, one finds that, by the break time $T_B = 1/\nu_2 \approx 34$ fs, the wave packet that results from the $^1A_1 \rightarrow {}^2A_1$ transition in ammonia has already sampled a fraction equal to about 3% of that part of phase space that is available to a thermal reference system ($F^* \approx 0.03$). For a spectroscopic excitation, the main restrictions derive from symmetry considerations. The spectroscopic wave packet can only expand in the subspace spanned by the totally symmetric wave functions. Since about 20% of the vibrational states that are located in the energy range of the $\tilde{X}$ band belong to the $A_1$ representation, one finds for the fractional occupation a value $F^{**} \approx 0.17$.

### B. The $\tilde{X}\ ^2B_3$ state of $C_2H_4^+$

The study of phase space sampling in the case of the $C_2H_4^+$ ion in its $\tilde{X}\ ^2B_3$ ground electronic state has already been studied by us in a previous paper.[17] We wish, however, to reexamine the situation along the present lines of thought and to correct a few inadequacies of the previous treatment. The information is derived from a photoelectron spectrum of $C_2H_4^+$ measured in a supersonic beam experiment by Pollard *et al.*[49] The density of states $D(E)$ has been calculated via the Beyer–Swinehardt counting algorithm,[2,39] which requires as an input the value of the normal frequencies of the twelve normal modes of the $C_2H_4^+$ cation. Only three of them ($\nu_2$, $\nu_3$, and $\nu_4$) are optically active and have been experimentally determined.[49] However, the twelve frequencies have been calculated *ab initio* (in the MP2/6-31 G* approximation).[50] The agreement between calculated and observed frequencies is excellent for $\nu_2$ and $\nu_3$, but not for the torsional mode $\nu_4$. It has been pointed out by Köppel, Cederbaum, and Domcke[51] that, in the particular case of the $C_2H_4^+$ cation, the values of the angle of twist and of the corresponding frequency are strongly influenced by the nonadiabatic interaction that exists between the first two electronic states of the ion. Highly correlated wave functions are necessary to obtain a reliable estimate for $\nu_4$. Working at the MP2 level is apparently not sufficient for the torsional mode. Therefore, the calculated value of $\nu_4$ has been replaced by the experimental measurement.

In the major part of the Franck–Condon envelope (say, up to an energy of about 0.7 eV), the calculated density of states function $D(E)$ can be approximately fitted to an exponential function $[D(E) \approx 0.0075 \exp(1.1\times10^{-3}\ E)$, with $E$ in wave number units], or to a Whitten–Rabinowitch function fulfilling condition (3.19) $[D(E) \approx 1.5\times10^{-15}(E+750)^4]$. Averaging the values provided by the two results, one finds for a thermal system, a fraction $F^*$ approximately equal to 0.1. For a spectroscopic excitation, this number should be modified mainly by symmetry considerations. The fraction of states that belong to the totally symmetric representation of the $D_2$ point group is about 0.4. Hence, $F^{**} \approx 0.25$. These numbers measure the sampling of phase space by time $T_B = 1.6\times10^{-13}$ s.

### C. The $\tilde{X}\,^2A''$ state of $C_2H_3F^+$

The first band of the photoelectron spectrum of vinyl fluoride has been studied by several authors.[52] Three progressions have been identified, leading to frequencies of 450, 1270, and 1550 $cm^{-1}$. Values for the other vibrational frequencies have been calculated by an *ab initio* method.[53] The results obtained at the UHF 6-31* G level were scaled by a factor equal to 0.89 and were used to estimate the density of states. The best fit to the function $D(E)$ is provided by a Whitten–Rabinovitch expression obeying condition (3.19). $[D(E)\approx 3.4\times 10^{-19}(E+1000)^5$, with $E$ in wave number units]. Other, less accurate, fits are also possible: $D(E)\approx 4.3\times 10^{-15}E^4$, and $D(E)\approx 0.018\exp(1.0\times 10^{-3}E)$.

Since the smallest splitting detected in the spectrum is of the order of 275 $cm^{-1}$, a value of $1.2\times 10^{-13}$ s can be estimated for the break time $T_B$. By that time, the wave packet has sampled a fraction $F^*$ of that part of phase space that is available to a thermal reference system equal to about 0.025. The situation is less clear for a spectroscopic excitation, but the main restrictions are again seen to derive from symmetry considerations. The spectroscopic wave packet can only expand in the subspace spanned by the totally symmetric wave functions. Since about 50% of the vibrational states that are located in the energy range of the band belong to the $A'$ representation, one finds that, for a spectroscopic reference system, the fractional sampling of phase space is about twice that found for a thermal system, i.e., $F^{**}\approx 0.05$.

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