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Intramolecular vibrational energy relaxation seen as expansion in phase space. I. Some experimental results for $H_2O^+(\tilde{X}\,^2B_1)$, $C_2H_4^+(\tilde{X}\,^2B_3)$, and $HCN^+(\tilde{B}\,^2\Sigma^+)$

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It has been shown by Heller that a nonstationary wave packet resulting from a Franck–Condon transition evolves on the potential energy surface of the final electronic state and propagates through phase space at a rate which can be determined from the autocorrelation function $|C(t)|^2 = |\langle\varnothing(0)|\varnothing(t)\rangle|^2$. Since $C(t)$ can be obtained by Fourier transformation of an optical spectrum $S(E)$, i.e., from an observable quantity, it is possible to derive from an experimental measurement information concerning the density operator of a so-called dynamical statistical ensemble (DSE). This density operator, denoted ρ^{av}, represents a statistical mixture of the eigenstates of the system with weights determined by the dynamics of the system. It becomes diagonal after a so-called break time $\mathscr{T}_B$. Its measure, according to a definition due to Stechel, can be interpreted as an effective number of states (denoted $\mathscr{N}$) that significantly contribute to the dynamics. The break time $\mathscr{T}_B$ represents the finite period of time allowed to expand in the phase space and after which no further progress can be made. Therefore, the number $\mathscr{N}_\infty$ of phase space cells which are accessed after a very long interval of time (or in practice after the break time) remains limited. Information on the validity of statistical theories of unimolecular reactions is contained in the fraction $\mathscr{F}$ of the available phase space which is eventually explored. In order to assess the representativity of the sampling, it is necessary to account for the selection rule which requires all the states counted in $\mathscr{N}_\infty$ to belong to the totally symmetric representation. It is also appropriate to estimate the role played by Fermi resonances and similar vibrational interactions which bring about energy flow into zero-order antisymmetric modes. A method to carry out the necessary partitionings is suggested. The functions $\mathscr{N}_T$ and $\mathscr{R}_T$, and the quantities $\mathscr{T}_B$, $\mathscr{N}_\infty$, $\mathscr{N}^*$, and $\mathscr{F}$ have been determined from experimental data in three cases. In each case, the rate $\mathscr{R}_T = d\mathscr{N}_T/dT$ starts from an initial value of zero, increases up to a maximum which is reached after a time of the order of 10^{-14} s, and then exhibits an overall decrease upon which oscillations are superimposed. For state $\tilde{X}\,^2B_1$ of H_2O^+, $\mathscr{T}_B \simeq 2.4\times10^{-14}$ s and $\mathscr{F}\simeq 0.3$. The wave packet never accesses that part of the phase space that corresponds to the excitation of antisymmetric vibrations. For state $\tilde{X}\,^2B_{3u}$ of $C_2H_4^+$, $\mathscr{T}_B \simeq 1.6\times10^{-13}$ s and $\mathscr{F}\simeq 5\times10^{-4}$. This fraction raises to 6×10^{-3} if measured with respect to the effectively available phase space. When the spectrum consists of a discrete part followed by a dissociation continuum, the method can be extended to study the behavior of the bound part of the wave packet only. This has been applied to state $\tilde{B}\,^2\Sigma^+$ of HCN^+ which is characterized by a very irregular spectrum. This case offers an example of complete occupation of phase space after a break time which is of the order of 2×10^{-13} s.

I. INTRODUCTION

The process commonly referred to as intramolecular vibrational energy relaxation is of crucial importance in chemical kinetics. Whether or not this relaxation is faster than chemical reaction determines the validity of the RRKM theory of unimolecular reactions.[1–5] In the present paper, we concentrate on the purely intramolecular process taking place in an isolated molecule initially excited by photon or electron impact under collision-free conditions.[2] The chemical activation experiments carried out by Rabinovitch, Kistiakovsky, and others[1,3] are therefore irrelevant for our purposes. In spite of the fundamental importance of the question, most of the kineticists usually dismiss the problem, simply by assuming that vibrational relaxation is due to unspecified anharmonic couplings among the zero-order normal modes. Recently, however, techniques of nonlinear mechanics applied to classical trajectory calculations have significantly contributed to understanding the mechanism of the relaxation.[6–10]

Experimentally, valuable information on the unimolecular decomposition of ionized molecules has come, first from photoion–photoelectron coincidence spectroscopy (PIPECO experiments),[11,12] then from multiphoton ionization.[13] This technique has shown that, at least in a vast majority of cases, there is no correlation between the yield of fragmentation and the vibronic structure of the molecular ion. In other words, this implies that the rate constants are

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function of the internal energy alone, i.e., that a statistical (microcanonical) approach is applicable.

Detailed spectroscopic studies have also been very fruitful. Laser excitation of molecular beams[14–18] is a field of active research. Statistical analysis of the distribution of level spacings, linewidths and intensities is also very promising,[19–24] but requires high-quality experimental data and preliminary classification of spectral lines according to the symmetry species.

In the present paper, we wish to carry out an analysis based on the autocorrelation function as an input data, i.e., an information which is much less sensitive to experimental uncertainties resulting, e.g., from finite energy resolution. It is based on a contribution of fundamental importance due to Heller and co-workers,[25–31] which offers a possibility of extracting the required information from experimental electronic spectra. A Franck–Condon transition leads to a nonstationary wave packet which evolves on the potential energy surface of the upper electronic state (Fig. 1). During this evolution, the wave packet undergoes flattening and distortion because of anharmonicity. It may even split up if anharmonicity is strong enough, e.g., because of the presence of a low energy dissociation asymptote. All of this has its counterpart in the phase and quantum Hilbert spaces and may be described as intramolecular vibrational relaxation. The procedure which will be investigated here is carried out in two sequential steps, viz., (A) transforming the spectrum into a so-called autocorrelation function $C(t)$; and (B) extracting the desired information from $C(t)$. Let us be more specific.

(A) First, the experimental spectrum $S_{\rm exp}(E)$ is converted by a Fourier transformation into an experimental correlation function $C_{\rm exp}(t)$:

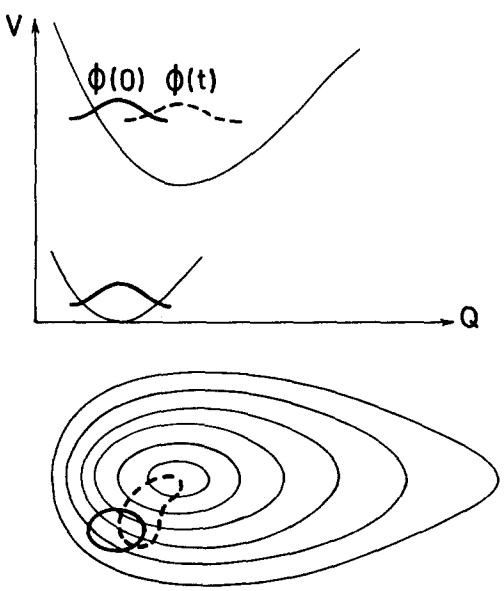

FIG. 1. A Franck–Condon transition leads to a wave packet ∅ which propagates on the potential energy surface of the upper electronic state. Top: cross section in a multidimensional surface. Bottom: two-dimensional representation in terms of a set of contours. Heavy line: initial position of the wave packet. Broken: displaced position at time t.

$$C_{\rm exp}(t) = \int_{-\infty}^{+\infty} S_{\rm exp}(E) e^{-iEt/\hbar} dE \Big/ \int_{-\infty}^{+\infty} S_{\rm exp}(E) dE. \tag{1.1}$$

To proceed further, one first assumes the validity of the Condon approximation, i.e., the transition moment is split into two parts: electronic and vibrational. This excludes strong vibronic coupling due to Jahn–Teller or Renner–Teller interactions, but does not exclude consideration of an electronically predissociated state.[32] Secondly, the rotational part of the correlation function is factorized away, in order to reduce the nuclear motion to a pure vibration. In addition, the correlation function has to be corrected for finite energy resolution and spin–orbit coupling effects. The appropriate procedures have been described in previous papers.[33–37] As a result, the experimental function $C_{\rm exp}(t)$ is transformed into a purely vibrational correlation function $C(t)$ which represents the time-dependent overlap integral between two vibrational wave functions:

$$C(t) = \langle \varnothing(0) | \varnothing(t) \rangle = \int_{-\infty}^{+\infty} S(E) e^{-iEt/\hbar} dE, \tag{1.2}$$

where $\varnothing(0)$ is the vibrational wave function of the initial state from which the Franck–Condon transition takes place, i.e., the vibrational ground state of the initial electronic state, and $\varnothing(t)$ is the wave packet at time t as it moves away from its initial position $\varnothing(0)$ on the potential energy surface of the final state.

There is a complete equivalence between the information contained in the corrected correlation function $C(t)$ and that contained in a new spectral function $S(E)$. The latter is a highly idealized concept since it corresponds to a well-resolved rotationless and spin-free spectrum. Unfortunately, the necessary corrections are approximate only, so that the quality of the function $C(t)$ which can be obtained in practice decreases with time. Usually, it can be determined only up to a time which is of the order of 100 or 200 fs at most. Thus, the method allows us to study the short-time dynamics only.

In general, the modulus of the correlation function $|C(t)|$ exhibits peaks that indicate when a substantial fraction of the wave packet revisits the original Franck–Condon region. For all practical purposes, the travelling wave packet can be imagined as a swarm of classical trajectories on a given potential energy surface. Numerous papers have appeared that study this motion on model potential energy surfaces,[25] or on potentials fitted to real-life molecules.[31,38–41] Methods to derive information on the characteristics of potential energy curves or surfaces,[34–37,42] or on molecular processes such as Fermi resonance and Duschinsky rotation,[43] or on unimolecular dissociation rate constants[44] have been given, but this approach is not pursued in the present paper.

(B) Once the correlation function has been obtained, the next step consists in relating the theoretical function $|C(t)|^2$ to a distribution in phase space. One has from Eq. (1.2):

$$|C(t)|^2 = \sum_i \sum_j \langle i|\varnothing(0)\rangle\langle\varnothing(0)|j\rangle\langle j|\varnothing(t)\rangle\langle\varnothing(t)|i\rangle$$
$$= \mathrm{Tr}[\rho(0)\rho(t)], \tag{1.3}$$

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where

$$\rho(0) = |\varnothing(0)\rangle\langle\varnothing(0)|$$

and

$$\rho(t) = |\varnothing(t)\rangle\langle\varnothing(t)| \tag{1.4}$$

are the density operators corresponding to the pure states $|\varnothing(0)\rangle$ and $|\varnothing(t)\rangle$ defined in Eq. (1.2).

Following the lines recently proposed by the Heller group,[26-30] one can then use the $|C(t)|^2$ function to obtain information on the phase-space distribution, on the rate $\mathscr{R}$ at which the wave packet sweeps out the phase space, on the effective number $\mathscr{N}$ of the phase-space cells occupied by the vibrational motion and, finally, on the degree of ergodicity of a dynamical process.

The paper is organized as follows. In Secs. II–V, we try to define more accurately the basic concepts and methods developed mainly by Heller *et al.*, and introduce among other things the concept of a dynamical statistical ensemble. Application to real systems is presented in Secs. VI–IX. The paper concludes with a discussion of the results and some general conclusions.

We have chosen to apply the method to three molecular ions for which autocorrelation functions derived from photoelectron spectra are available.[33,35,37,45] From an experimental point of view, reaction dynamics is in some respects more easily studied in beams of charged particles than in neutral systems. Our goal is to establish a link between the ultrashort time scale which can be studied by the present technique and the dissociations that take place on the time scale of ion extraction for which a wealth of experimental information exists[11-13,46] in order to obtain a unified view on intramolecular processes.

II. A MEASURE OF QUANTUM ERGODICITY

Let us consider a system in a pure but nonstationary quantum state:

$$\varnothing(t) = \sum_k a_k(t)|k\rangle, \tag{2.1}$$

where $|k\rangle$ are the eigenfunctions of the Hamiltonian H of the system. For simplicity, we restrict ourselves in this section to the nonstationary states built from bound state eigenfunctions only. First, we introduce some quantitative measure to characterize the dynamical process. A very natural way to do this has been proposed by Stechel and Heller.[27-30] We reformulate their theory in order to clarify the physical meaning of the quantities $\mathscr{N}$ and $\mathscr{R}$ introduced by these authors to describe the phase space flow due to the evolution of a nonstationary pure state.

With every system described by the density operator ρ, Stechel and Heller associate a positive number μ defined by

$$\mu^{-1} = \mathrm{Tr}(\rho^2). \tag{2.2}$$

To clarify the physical meaning of μ, we note at first that for a pure state [Eq. (1.4)] the measure μ is equal to 1 at any time, making it thus irrelevant for dynamical problems. Therefore, to characterize the time evolution of a nonstationary pure state, we consider the following density operator:

$$\rho^{\mathrm{av}} = (1/T)\int_0^T \rho(t)dt. \tag{2.3}$$

It is important to realize that ρ^{av} is no longer the density operator of a pure state, but that of a statistical ensemble. Its physical meaning will now be analyzed from two different points of view.

From Eqs. (2.1) and (2.3), one gets the following expression for ρ^{av}:

$$\rho^{\mathrm{av}} = \sum_k p_k |k\rangle\langle k| - (i/T) \times \sum_{k\neq n} a_k a_n^* \left[(e^{i\omega_{nk}T} - 1)/\omega_{nk} \right] |k\rangle\langle n|, \tag{2.4}$$

where

$$\omega_{nk} = (E_n - E_k)/\hbar \tag{2.5}$$

and

$$p_k = |a_k|^2. \tag{2.6}$$

In a spectroscopic experiment, the latter quantities are the usual Franck–Condon factors. (Obviously, $\Sigma_k p_k = 1$.)

The quantum measure of this ensemble is given by

$$\mu^{-1} = \sum_k p_k^2 + (4/T^2) \times \sum_{k>n} p_k p_n \left[(1 - \cos\omega_{nk}T)/\omega_{nk}^2 \right]. \tag{2.7}$$

The operator ρ^{av} has a clear physical meaning in the long-time limit, i.e., when

$$T \gg T_B = \max_{n,k} (8p_n p_k/\omega_{n,k}^2)^{1/2}. \tag{2.8}$$

When T is large enough ($T \gg T_B$), ρ^{av} becomes diagonal. It describes a statistical mixture of the eigenstates of H with weights given by the Franck–Condon factors. In the long-time limit, μ simplifies to

$$\mu^{-1} = \sum_k p_k^2. \tag{2.9}$$

As explained by Stechel,[28] there is a difference between the measures defined by Eqs. (2.2) and (2.9) which has been disregarded here for simplicity. Thus, the measure μ increases from an initial value of 1 (pure case) to a final value given by Eq. (2.9). It also follows from the same equation that in the long-time limit, μ can be interpreted as an effective number of states significantly contributing to the dynamics.[26-30,47] The simplest way to see this is to consider the particular case where the system can be found with equal probabilities in N different eigenstates of H. Equation (2.9) then simply gives $\mu = N$. In the case of unequal probabilities, μ varies between 1 and N. It adopts a value of 1 when the dynamics is dominated by a single state and reaches a maximum value of N when all the states participate on an equal footing in the dynamics.

To get further insight into the physical meaning of ρ^{av}, let us study the time evolution of the system in the usual quantum Hilbert space. At a given time, the dynamical state of the system is represented by a state vector in an N-dimensional complex or $2N$-dimensional real linear space parame-

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trized by the coefficients a_k defined in Eq. (2.1). The normalization condition constrains the vector to sweep a $(2N-1)$-dimensional sphere in the $2N$-dimensional real space. Furthermore, the set of points $\{e^{i\varphi}a_1, e^{i\varphi}a_2, \ldots, e^{i\varphi}a_N\}$ with $(0 \leqslant \varphi < 2\pi)$ is understood to define a single state. In this way, one arrives at the so-called complex projective sphere, as a manifold whose points are in one-to-one correspondence with quantum states.

Coming back to the physical meaning of ρ^{av}, we partition the obtained manifold into small cells of equal measure and rewrite Eq. (2.3) as

$$\rho^{av} = \lim_{\Delta t \to 0} \sum_{\lambda=0}^{M} \rho(\lambda \Delta t)(\Delta t/T) \tag{2.10}$$

with $T = M\Delta t$. At every moment $\lambda \Delta t$, the representative point of the system is located in one of the cells. Gathering together all the terms corresponding to the same cell α, one can write

$$\rho^{av} = \sum_{\alpha} p_\alpha \rho^{(\alpha)} \tag{2.11}$$

with

$$\sum_{\alpha} p_\alpha = 1 \tag{2.12}$$

and

$$\rho^{(\alpha)} = \sum_{k,l} \langle a_k a_l^* \rangle_\alpha \, |k\rangle\langle l| . \tag{2.13}$$

The symbol $\langle a_k a_l^* \rangle_\alpha$ denotes an average within the cell α. In Eqs. (2.11) and (2.12), the summation runs over all the cells visited during the evolution.

Hence, ρ^{av} is again seen to be a density operator of a statistical ensemble in which the weights of the different states are determined by the dynamics of the system. The weights will be greater for those cells in which the system spends more time on the average. One also sees that the cells that are not revisited by the system frequently enough cannot contribute to ρ^{av} in the long-time limit.

In the remainder of this paper, we refer to this ensemble as the dynamical statistical ensemble (DSE).

III. PHASE-SPACE FLOW

In studies on quantum ergodicity it is very instructive to use the Wigner formulation of quantum mechanics, according to which the time evolution of the quantum system can be viewed as a phase-space flow associated with a phase-space distribution $\rho(\mathbf{p},\mathbf{q},t)$ given by

$$\rho(\mathbf{p},\mathbf{q},t) = (\pi h)^{-f} \int_{-\infty}^{+\infty} e^{2i\mathbf{p}\cdot\mathbf{s}/\hbar} \varnothing^*(\mathbf{q}+\mathbf{s},t)\varnothing(\mathbf{q}-\mathbf{s},t)d\mathbf{s}, \tag{3.1}$$

where f is the number of degrees of freedom of the system. Following Stechel and Heller,[27-30] we can now define a phase-space counterpart of the quantum measure μ by

$$\mathcal{N}^{-1} = h^f \mathrm{Tr}[\rho^2(\mathbf{p},\mathbf{q})]$$

$$= h^f \int\int d\mathbf{p}\, d\mathbf{q}\, \rho^2(\mathbf{p},\mathbf{q}). \tag{3.2}$$

Since for a system with f degrees of freedom the function $\mathrm{Tr}[\rho^2(\mathbf{p},\mathbf{q})]$ has the dimension of (action)$^{-f}$, i.e., the dimension of an inverse volume in phase space, $\mathcal{N}$ can be interpreted as an effective number of elementary phase-space cells of volume h^f occupied by $\rho(\mathbf{p},\mathbf{q})$. Taking into account the fact that every pure quantum state occupies one elementary phase-space cell, we see that μ and $\mathcal{N}$ have essentially the same physical meaning, i.e.,

$$\mu = \mathcal{N} \tag{3.3}$$

(a much more elaborate discussion has been given by Stechel[28]).

In order to study the time evolution of the system according to the discussion of the previous section, we introduce the DSE characterized by an averaged distribution

$$\rho^{av}(\mathbf{p},\mathbf{q},T) = (1/T)\int_0^T \rho(\mathbf{p},\mathbf{q},t)dt \tag{3.4}$$

and its measure

$$\mathcal{N}_T^{-1} = h^f \int\int d\mathbf{p}\, d\mathbf{q} [\rho^{av}(\mathbf{p},\mathbf{q},T)]^2, \tag{3.5}$$

where $\mathcal{N}_T$ represents the effective number of phase-space cells occupied by $\rho^{av}(\mathbf{p},\mathbf{q},T)$.

$\mathcal{N}_T$ is related in a simple fashion to the correlation function $C(t)$ and can thus be easily obtained from the experimental spectra.

Substituting Eqs. (3.4) and (1.3) into Eq. (3.5), one arrives at[30]

$$\mathcal{N}_T^{-1} = (2/T)\int_0^T dt(1-t/T)\,|C(t)|^2. \tag{3.6}$$

This equation plays a fundamental role in what follows. At very short times, one deals with a pure case:

$$\lim_{T\to 0} \mathcal{N}_T = 1. \tag{3.7}$$

Since we want to use $\mathcal{N}_T$ to characterize an intramolecular relaxation, consideration of its asymptotic value is of prime importance. The quantum measure in the long-time limit can be readily obtained from Eqs. (2.9) and (3.3):

$$\mathcal{N}_\infty^{-1} = \sum_k p_k^2. \tag{3.8}$$

It can also be calculated with the help of the correlation function

$$(\mathcal{N}_\infty)^{-1} = \lim_{T\to\infty} (2/T)\int_0^T (1-t/T)\,|C(t)|^2 dt \tag{3.9}$$

$$= \lim_{T\to\infty} (1/T)\int_0^T |C(t)|^2 dt. \tag{3.10}$$

Equations (3.8)–(3.10) provide three different ways to calculate $\mathcal{N}_\infty$ which, in principle, are equivalent. A fourth one will be presented in the next section. For a numerical study of experimental data, they provide interesting checks. The spectra may be poorly resolved, so that a determination of individual Franck–Condon factors may be very difficult. This is especially the case at high energies close to the dissociation limit where information concerning the validity of statistical theories of unimolecular reactions is seeked. The use of Eq. (3.9) enables one to bypass the measurement of Franck–Condon factors. However, the quality of experi-

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mentally available correlation functions decreases with time, so that the limits may have to be obtained by extrapolation. In practice, Eq. (3.10) is found not to be very useful for an extrapolation, and a more practical procedure to do this will be suggested in the next section.

Following Heller,[30] we now introduce the quantity $\mathscr{R}_T$:

$$\mathscr{R}_T = d\mathscr{N}_T/dT = (1/2)\int_0^T (1-2t/T)\,|C(t)|^2 dt \Big/ \left[\int_0^T (1-t/T)\,|C(t)|^2 dt\right]^2. \tag{3.11}$$

From the discussion given in Sec. II, it follows that $\mathscr{R}_T$ represents the rate of growth of the phase space volume occupied by the DSE, i.e., the volume regularly revisited by the wave packet during its evolution. The present interpretation of $\mathscr{R}_T$ is thought to represent more adequately its physical meaning than that proposed in Ref. 30 in terms of a rate of phase-space exploration.

At very short times, the rate increases linearly with time and

$$\lim_{T\to 0} \mathscr{R}_T = 0. \tag{3.12}$$

In the long-time limit

$$\lim_{T\to\infty} \mathscr{R}_T = \left[2\int_0^T |C(t)|^2 dt\right]^{-1}. \tag{3.13}$$

A more detailed discussion of the properties of $\mathscr{R}_T$ has been given in Ref. 30.

IV. THE RELAXATION TIME

Of prime importance in chemical kinetics is the lapse of time which characterizes the relaxation from the initially prepared distribution. A very useful concept has been introduced by Heller.[30] After a so-called break time $\mathscr{T}_B$, the effective number of cells occupied by the DSE is thought to have reached its asymptotic value $\mathscr{N}_\infty$. In other words, the DSE cannot significantly increase its phase space volume after the break time, which is given by

$$\mathscr{T}_B \simeq h/\delta, \tag{4.1}$$

where δ is the smallest energy gap between two optically active vibrational levels (i.e., having nonzero Franck–Condon factors in the optical spectrum). This concept turns out to be extremely useful, but requires some clarification.

(1) First of all, we have to specify the meaning of a relaxation time in a nondissipative system. Strictly speaking, an isolated mechanical system cannot relax.[49] The answer is that this concept really applies to the relaxation of the DSE introduced in Sec. II to its equilibrium state described by the long-time limit density operator

$$\rho^{\mathrm{av}} = \sum_k p_k |k\rangle\langle k|. \tag{4.2}$$

This relaxation leads to an increase of the quantum measure $\mathscr{N}_T$ from 1 (at time $T=0$) to its maximum value $\mathscr{N}_\infty$ given by Eqs. (3.8)–(3.10).

Equation (2.7) shows that the relaxation is caused by the multiplicative factor T^{-2} in front of the sum. The dephasing of the different cosine terms in this sum is of minor importance because all of these terms are positive. At this point, it should be stressed once more that the relaxation in question should be understood as the relaxation of the corresponding DSE. Therefore, it will occur even in a two-level system.

(2) The break time $\mathscr{T}_B$ defined in Eq. (4.1) is a characteristic time scale of the relaxation process. It can be understood as a time at which condition (2.8) is approximately fulfilled. To see this, we note that one has $p_n p_k \leqslant 0.25$. The equality obtains when only two levels are initially populated with equal intensities (i.e., $p_k = p_n = 0.5$). Substituting this into Eq. (2.8) leads to

$$T_B < \sqrt{2}/\min_{k,n} \omega_{kn} = h/\pi\sqrt{2}\delta \simeq 0.225\mathscr{T}_B. \tag{4.3}$$

(3) Since $\mathscr{N}_T$ tends to $\mathscr{N}_\infty$ as $T\to\infty$ asymptotically only, we have to introduce an arbitrary parameter β in our definition of the characteristic relaxation time to obtain a finite value ($\beta < 1$). The relaxation kinetics is then characterized by the time $\mathscr{T}_\beta$ necessary for $\mathscr{N}_T$ to reach the value $\beta\mathscr{N}_\infty$:

$$\mathscr{N}_{\tau_\beta} = \beta\mathscr{N}_\infty.$$

A concrete value of β is not of crucial importance, because it is the order of magnitude of the relaxation time which matters. We note, however, that there exist special cases where the choice of β can make a difference. This will be the case, e.g., for a system whose spectrum consists of groups of quasi-degenerate levels which are well separated from one another. In this case relaxation is characterized by two very different time scales, with fast intergroup and slow intragroup relaxation. The function $\mathscr{N}_T$ has now two regimes and one has to decide beforehand whether or not the slow intragroup relaxation is important for the process in question.

(4) From Eqs. (2.7), (2.9), (3.3), and (3.8), one can estimate an upper bound for the difference between $\mathscr{N}_T^{-1}$ and its asymptotic limit $\mathscr{N}_\infty^{-1}$.

$$\left|\mathscr{N}_T^{-1} - \mathscr{N}_\infty^{-1}\right| \leqslant (8/T^2)\sum_{k>n} p_k p_n/\omega_{nk}^2 \tag{4.4}$$

Although the right-hand side of Eq. (4.4) depends both on the energy spectrum (frequencies) and on the initial preparation (Franck–Condon factors), it follows from the discussion in paragraphs (2) and (3) that, unless there exists a gross disparity between the distribution of the frequencies and that of the Franck–Condon factors, it reaches a negligible value at time $\mathscr{T}_B$. It has to be noted that $\mathscr{T}_B$ also depends on the initial preparation, but somewhat indirectly, i.e., through the not very explicit requirement that δ be the minimum energy gap between two adjacent levels both having nonzero Franck–Condon factors. Thus, the existence of closely packed levels can significantly delay the relaxation only if these levels are significantly populated by the excitation process.

(5) The previous ideas can be used to derive an extrapolation formula for $\mathscr{N}_T$. This is very useful, since in practice the quality of the experimental data may not be sufficient to

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calculate the function $\mathcal{N}_T$ up to the break time. Consider a bound state with a spectrum represented by the function

$$S(E) = \sum_i p_i \delta(E - E_i). \tag{4.5}$$

Substituting into Eq. (1.2), one gets

$$|C(t)|^2 = \sum_i \sum_j p_i p_j \cos[(E_i - E_j)t/\hbar]. \tag{4.6}$$

Elementary algebra shows that the following approximate relationship exists between the function $\mathcal{N}_T^{-1}$ and its first derivative evaluated at half of the break time:

$$\mathcal{N}_\infty^{-1} = \sum_i p_i^2 \simeq (\mathcal{N}_{0.5\mathcal{T}_B})^{-1} + 0.25\mathcal{T}_B \left(\frac{d}{dt}\mathcal{N}_T^{-1}\right)_{0.5\mathcal{T}_B} \tag{4.7}$$

The validity of this approximate formula will later on be checked on actual systems.

In summary, the simple formula (4.1) can be used in many cases instead of the more accurate condition (2.8). Moreover, it gives rise to the useful extrapolation formula (4.7).

V. THE FRACTION OF THE PHASE SPACE OCCUPIED BY THE DSE

In order to get some deeper insight into the dynamics of the DSE introduced in Sec. II, it is instructive to consider the fraction $\mathcal{F}$ of the phase space occupied by the DSE in the long-time limit:

$$\mathcal{F} = \mathcal{N}_\infty / \mathcal{N}^*, \tag{5.1}$$

where $\mathcal{N}^*$ denotes the number of the phase-space cells that are *a priori* available for a given dynamical process. Its value depends on our *a priori* knowledge about the system in question. This quantity, introduced by Stechel and Heller,[27–30,47] is very useful in studies concerning the validity of the usual statistical theories, such as RRKM, for which the only restriction taken into account concerns the internal energy of the system. In this case, $\mathcal{N}^*$ is equal to the number of all energetically available phase-space cells. However, we improve our understanding of the dynamics of the DSE when we incorporate additional *a priori* information and investigate its effects on $\mathcal{N}^*$ and $\mathcal{F}$. For example, if the additional *a priori* information results in $\mathcal{F} \simeq 1$, then it seems reasonable to conclude that the dynamics is ergodic within the existing constraints. This also implies that our knowledge about the system is virtually complete and cannot be essentially improved. As shown by Levine *et al.*,[47,48] $\mathcal{F}$ measures the completeness of our *a priori* information.

Information concerning the excitation process can be incorporated in the form of a spectral envelope.[26–30,47] This is done in Sec. V A. The quantum nature of the dynamics also imposes some additional restrictions on the value of $\mathcal{N}^*$. It turns out that the number of the phase-space cells occupied by the DSE in the long-time limit under fully chaotic conditions never exceeds 1/3 of the total number of energetically available phase-space cells.[27–30,47] It is natural to accept this as an *a priori* information, as shown in Sec. V B. In studies of intramolecular processes initiated by a coherent excitation, it is also natural to take into account an *a priori* information about the symmetry properties which lead to selection rules.[29,30,47] This is done in Sec. V C. Finally, we introduce in Sec. V D several measures appropriate for an investigation of the dynamics within different homogeneous subspaces of the quantum Hilbert space characterized, e.g., by different types of symmetry or excitation. We now examine all this in more detail.

A. Excitation constraint

As shown by Heller,[26–30] a natural way to take into account the constraint imposed on $\mathcal{N}^*$ by the excitation process is to introduce the envelope $S_T(E)$ of the spectral distribution $S(E)$. The latter describes the fully resolved spectrum and contains as much of the information as the correlation function determined up to an infinite time. On the other hand, $S_T(E)$ represents the fictitious spectrum obtained as the Fourier transform of a correlation function truncated after some time T. Physically, this amounts to studying the dynamics during a short time only. The function $S_T(E)$ is called the envelope of the genuine spectrum $S(E)$. (More exactly, it is a smoothed version of it.) The envelope $S_T(E)$ can be easily calculated[30]

$$S_T(E) = \sum_k p_k \Omega_T(E - E_k), \tag{5.2}$$

where

$$\Omega_T(E - E_k) = \sin[(E - E_k)T/h]/[\pi(E - E_k)]. \tag{5.3}$$

Note that the profile of this envelope depends on the choice of the truncation time T. Heller has proposed to consider the function $S^*_T(E)$ determined for a particular time T^* corresponding to the first minimum of the correlation function, at the end of the initial decay and before any recurrence. To calculate $\mathcal{N}^*$, we now have to choose a reference spectrum reflecting our *a priori* information about the fully ergodic situation under the constraint imposed by $S^*_T(E)$. A natural choice is a spectrum with Franck–Condon factors given by

$$p_n^* = S^*_T(E_n) / \sum_k S^*_T(E_k), \tag{5.4}$$

where indices n and k run over all states within the envelope, both optically active and inactive. The information about selection rules and dynamical details (i.e., those reflected in the numerous peaks of the correlation function $|C(t)|$) is totally absent from the reference spectrum. Thus, the physical meaning of the constraint imposed by $S^*_T(E)$ can be roughly understood as a way to take into account an *a priori* information about the energy spread of the initially prepared wave packet.

Several methods can be used to calculate $\mathcal{N}^*$:

(1) The first method is based on the use of Franck–Condon factors corresponding to the envelope $S^*_T(E)$ [Eq. (5.4)]. Substituting into Eq. (3.8), one has

$$(\mathcal{N}^*)^{-1} = \sum_n (p_n^*)^2. \tag{5.5}$$

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This method implies the calculation of the smoothed spectral envelope $S^*_T(E)$ and a knowledge of the energies of all the levels within this envelope.

(2) Heller also proposes[30] another formula to estimate $\mathcal{N}^*$:

$$\mathcal{N}^* = \mathcal{R}^* \mathcal{T}_B, \tag{5.6}$$

where $\mathcal{R}^*$ is the rate at time $\mathcal{T}^*$ (i.e., the time at which $|C(t)|$ admits its first minimum), but we disagree with this equation for several reasons. Heller's derivation is

$$\begin{aligned}\mathcal{N}^* &= \left[\sum_n (p_n^*)^2\right]^{-1} \simeq \left|\int_{-\infty}^{+\infty} [[S^*_T(E)]^2 / D^*_T(E)]dE\right|^{-1} \\ &\simeq h\langle D^*\rangle / h\int_{-\infty}^{+\infty} [S^*_T(E)]^2 dE \\ &\simeq \mathcal{T}_B \mathcal{R}^*. \end{aligned} \tag{5.7}$$

First, one should note that the quantity $\langle D^*\rangle$ defined in the second step of the derivation has the meaning of the density of states at some unspecified point within the energy envelope and, strictly speaking, cannot be interpreted as an average value of the function $D(E)$. Moreover, even when $\langle D^*\rangle$ is approximately equal to the average value of $D(E)$, the product $h\langle D^*\rangle$ is not $\mathcal{T}_B$ as defined in Eq. (4.1). The break time is equal to h/δ, where δ is the smallest energy gap between two optically active levels and not the average quantity $\langle D^*\rangle^{-1}$. Finally, although it can be demonstrated[30] that, at any time T,

$$h\int_{-\infty}^{+\infty} [S_T(E)]^2 dE = 2\int_0^T |C(t)|^2 dt, \tag{5.8}$$

Eq. (3.13) cannot be invoked to equate the left-hand side of Eq. (5.8) with $(\mathcal{R}^*)^{-1}$. This would be possible only in the long-time limit, after many recurrences, and certainly not at a time as short as T^*.

However, it is possible to retain the general philosophy of the argument and to calculate the denominator of Eq. (5.7) in another way. Since time T^* is very short (usually a few femtoseconds), the dynamics need be followed during a very short lapse of time. It is then possible to set up crude models which give a useful description of the correlation function up to a short time only. These models will later on be found to be useful in other connections as well. A natural choice for an empirical function to describe the short-time behavior of the correlation function of a bound system is

$$|C(t)|^2 \simeq 0.5(1+\gamma) + 0.5(1-\gamma)\cos\omega t, \tag{5.9}$$

where γ is the value reached by $|C(t)|^2$ at its first minimum, i.e., at a time $T^* = \pi/\omega$. Then,

$$2\int_0^{T^*} |C(t)|^2 dt \simeq (1+\gamma)T^*. \tag{5.10}$$

Substituting into Eq. (5.7), one finally obtains the following estimate for $\mathcal{N}^*$

$$\mathcal{N}^* \simeq h\langle D^*\rangle/(1+\gamma)T^* \tag{5.11}$$

(3) A third estimate of $\mathcal{N}^*$ can be derived as follows. The time T^* at which $|C(t)|^2$ reaches its first minimum is approximately equal to twice the time needed for the wave packet to move a distance equal to its width (called "dephasing time" by Bixon and Jortner[50]):

$$T^* \simeq 2\hbar/\Gamma, \tag{5.12}$$

where Γ is the energy spread of the wave packet. Then, from Eq. (5.11),

$$\mathcal{N}^* \simeq \langle D^*\rangle \Gamma\pi/(1+\gamma) \simeq \langle D^*\rangle\Gamma \tag{5.13}$$

since $0 \leqslant \gamma \leqslant 1$. If the value $\langle D^*\rangle$ is approximately equal to the average value of $D(E)$, then the factor $\langle D^*\rangle\Gamma$ represents the number of states (optically active and inactive) within the energy width of the wave packet.

B. Quantum constraint

In spectroscopic problems, when the number of final states is large, one deals with the so-called external case described by Brody *et al.*[51] This means that one studies the statistics of transition strengths between one (external) state $|c\rangle$ which is treated nonstatistically and a *large* group of d states $|i\rangle$ which are supposed to be statistical in nature. This assumption is very natural when the external state significantly differs from the statistical state $|i\rangle$. In this case, the whole transition probability is fragmented into many small parts and it is then reasonable to expect that the latter can be treated statistically.[47] In the statistical theory of spectra based on the properties of the matrix Gaussian orthogonal ensemble (GOE), or in the maximum entropy formalism, it is shown[20,22-24,27-29,47,51] that the distribution function for the transition probabilities (Franck–Condon factors in our case) for the external case with one external vector $\langle c\rangle$ is given by the Porter–Thomas formula

$$\rho_p(x) = (2\pi\langle p\rangle x)^{-1/2}\exp(-x/2\langle p\rangle) \tag{5.14}$$

with

$$\langle p\rangle = (1/d)\sum_{n=1}^{d} p_n \tag{5.15}$$

thus, corresponding to the usual χ_1^2 distribution. It should be noted that formula (5.14) does not take into account the smooth overall variation of the intensities with energy given by the spectral envelope. When applying Eq. (5.14) to the experimental data, one usually supposes that it is possible to take into account the smooth overall variation of the intensities with energy by using, instead of the globally averaged value $\langle p\rangle$ in Eq. (5.14), the locally averaged value which depends on E.[27-29,47]

Thus, we shall define a reference spectrum describing the fully ergodic dynamics under constraints imposed by the excitation process as a spectrum whose Franck–Condon factors are characterized by the envelope $S^*_T(E)$ and by the χ_1^2-type fluctuations of transition probabilities with respect to this envelope. These fluctuations are of quantum origin. It has been shown[27-30,47] that they reduce the number of the *a priori* accessible phase-space cells by a factor of 3. Thus, for the case in question, the number $\mathcal{N}^*_{QE}$ of phase-space cells which are *a priori* available for a given excitation process is given by

$$\mathcal{N}^*_{QE} = \mathcal{N}^*/3, \tag{5.16}$$

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where the subscript QE stands for "quantum ergodic" and the asterisk denotes an *a priori* estimate.

It is important to note that, when the number of states participating in the dynamics is not large enough, the present argument cannot be applied. Consider, e.g., the limiting case where the spectrum consists of a single line (i.e., a transition between two identical potential energy surfaces). One then has

$$\mathcal{N}_\infty = \mathcal{N}^* = \mathcal{N}^*_{\mathrm{QE}} = 1. \tag{5.17}$$

C. Symmetry constraint

When the dynamical process in question is initiated by a coherent excitation, it is natural to incorporate into our *a priori* knowledge the information about the symmetry properties of the transition operator and of the system. In the examples studied below, this information takes the form of the usual selection rules resulting from the Condon approximation.[52] This implies that all the states that are counted in $\mathcal{N}_\infty$ and which appear in Eqs. (2.1), (2.6), and (3.8) all belong to the totally symmetric representation of the molecular point group.

In contradistinction, all the states, active or inactive, whatever the representation they belong to, are counted in $\mathcal{N}^*$. Since the wave packet can only visit those portions of Hilbert space where the eigenfunctions it is made of are localized,[30] it is appropriate to compare $\mathcal{N}_\infty$ not with $\mathcal{N}^*$, but with a smaller number $\mathcal{N}^*_S$ obtained when one takes into account states that belong to the totally symmetric representation only.

It has been proved[53] that, as the energy increases, the occurrence of the various symmetry species in the spectrum rapidly equilibrates so that, at internal energies of the order of about twice the zero-point energy, the number of states that belong to a particular nondegenerate representation is the same for each representation.

D. Measures $\xi^{(\kappa)}$ and partitioning

The measures μ and $\mathcal{N}$ previously defined are very convenient when one studies the dynamics in the whole Hilbert space or in one of its subspaces determined by some of the constraints discussed above. However, they become inconvenient when one wants to compare the relative dynamical importance of different subspaces characterized, e.g., by different types of symmetry or excitation. To see this, consider two nonoverlapping subspaces of the Hilbert space, L_1 and L_2. The measures $\mu(L_i)$ corresponding to L_i are given by

$$[\mu(L_i)]^{-1} = \sum_{k\in L_i} \bar{p}_k{}^2, \tag{5.18}$$

where the quantities $\bar{p}_k$ are renormalized Franck–Condon factors:

$$\bar{p}_k = p_k / \sum_{k\in L_i} p_k. \tag{5.19}$$

It can be shown that $\mu(L_1 + L_2) \leqslant \mu(L_1) + \mu(L_2)$, i.e., in general, μ is not additive with respect to partitioning the Hilbert space into nonoverlapping subspaces and thus cannot serve as a measure. In order to partition μ of $\mathcal{N}$ into contributions corresponding to different types of states, one has to introduce some other measures, additive with respect to the partitioning of the Hilbert space into nonoverlapping subspaces. This can easily be done by associating with each quantum state $|n\rangle$ some positive number ξ_n, a natural choice being

$$\xi_n^{(\kappa)} = p_n^\kappa. \tag{5.20}$$

The choice of the appropriate value of the power κ is dictated by the problem at hand. For example, $\kappa = 0$ defines a measure which is entirely independent of the dynamics. It gives the total number of states participating in the dynamics regardless of their relative importance. To take into account the relative dynamical importance of different states, one has to introduce Franck–Condon factors, i.e., to use measures with $\kappa > 0$. The measure with $\kappa = 1$ (i.e., the use of Franck–Condon factors normalized to unity) allows one to compare the overall probability of finding the system in different subspaces but says nothing about the type of dynamics within each subspace. The simplest measure which gives this information is $\xi^{(2)}$

$$\xi_L^{(2)} = \sum_{k\in L} p_k^2. \tag{5.21}$$

The more irregular the distribution of Franck–Condon factors, the more regular the corresponding dynamics and the larger the value of $\xi^{(2)}$. [For the most irregular distribution ($p_i = \delta_{ik}$), one has $\xi^{(2)} = 1$; for the most regular case, ($p_1 = p_2 = \ldots = p_N$), one has $\xi^{(2)} = 1/N$.] Therefore, $\xi^{(2)}$ can be partitioned into contributions corresponding to different types of states; it can be used to measure and compare the degree of regularity of dynamics within different subspaces. Comparing *a priori* and experimental values of $\xi^{(2)}$ within different subspaces allows us to decide whether or not all *a priori* available different types of states are represented in the wave packet on equal footing, i.e., whether or not our sampling is representative enough to guarantee the success of a statistical approximation.

In summary, the crux of the matter results from the fact that what one has to partition is not simply a number of cells (or of quantum states) but an *effective* number of states that significantly contribute to the dynamics, i.e., an average weighted by occupation probabilities. Compare Eqs. (2.2), (2.9), and (5.21) with the well-known relationship $\langle A \rangle = \mathrm{Tr}(\rho A)$. One sees that $\xi^{(2)} = \mathrm{Tr}(\rho^2)$ represents an average density, whereas its inverse $\mu = [\mathrm{Tr}(\rho^2)]^{-1} = \mathcal{N}$ is proportional to an average volume in phase space. Obviously, the same partitioning cannot be simultaneously additive for a quantity and its inverse. In the present paper, measure (5.21) has been chosen because of its close connection with the experimentally derivable quantities μ and $\mathcal{N}$ discussed in the previous sections, but it should be noted that other choices of measures are also possible. One of the best known is

$$\xi_n^S = p_n \ln p_n \tag{5.22}$$

which arises in the information theoretic approach to intramolecular dynamics.[48] We leave it for further work.

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VI. THE $\tilde{X}^2B_1$ STATE OF H_2O^+

The photoelectron spectrum of the ground state of H_2O^+ has been determined many times,[37,45,54–56] the best one to data being that recorded by Reutt *et al.*[37] Since the initial ($\tilde{X}\ ^1A_1$) and final ($\tilde{X}\ ^2B_1$) states are characterized by very similar geometries, the spectrum is very simple and consists of an intense (000→000) transition followed by two progressions involving excitation of the two totally symmetric modes ν_1 and ν_2. Autocorrelation functions have been determined in two different laboratories.[37,45] They are given in Fig. 2. From these, the functions $\mathcal{N}_T$ and $\mathcal{R}_T$ have been determined by numerical integration [Eqs. (3.6) and (3.11)].

Results are given in Fig. 2. The value of the break time is easily determined from the spectra. One finds $\mathcal{T}_B = \nu_2^{-1} = (2.4 \pm 0.1)10^{-14}$ s. This value agrees with that derived from the more detailed criterion (2.8). The rate $\mathcal{R}_T$ starts from a value of zero and increases up to a maximum of about 8.6×10^{13} cells s^{-1}. The maximum is reached at time $T^*(\simeq 5.5$ fs), when the correlation function goes through a minimum. This is easily understandable. The initial motion of the center of the wave packet is a stretch away from the Franck–Condon region, during which it explores portions of phase space which are new to it. However, the first recurrence in the correlation function is associated with a return to the original region, which implies that the packet revisits portions of phase space that have already been previously occupied. The rate decreases gradually and is seen to drop to a very low value at the break time $\mathcal{T}_B$. That no further progress in phase space exploration is possible after time $\mathcal{T}_B$ is confirmed by a study of $\mathcal{N}_T$. This function levels off at a maximum value $\mathcal{N}_\infty = 1.83 \pm 0.05$ which is reached at time $\mathcal{T}_B$. This asymptotic value can be checked with that derived from Franck–Condon factors [Eq. (3.8)]. The latter have been determined by three different groups[37,55,56] and lead to values of 1.72, 1.76, and 1.97, in satisfactory agreement with those obtained from the correlation function. The extrapolation formula (4.7) is found to work well since it leads to a value of 1.76 ± 0.06 for $\mathcal{N}_\infty$.

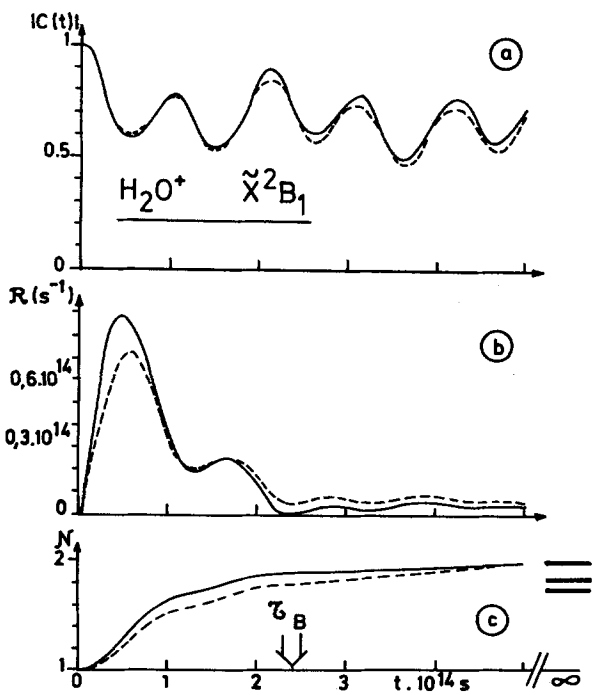

FIG. 2. (a) Autocorrelation function of state $\tilde{X}\ ^2B_1$ of H_2O^+. Solid line: results taken from Ref. 37. Dashed: results taken from Ref. 45. (b) Rate of propagation in phase space (in s^{-1}). (c) Number of phase-space cells visited as a function of time. $\mathcal{T}_B$ = break time determined from Eq. (4.1). Extreme right: asymptotic value $\mathcal{N}_\infty$ determined from experimental Franck–Condon factors.

All the states that contribute to $\mathcal{N}_\infty$ necessarily belong to the totally symmetric representation A_1 of the C_{2v} point group. However, in order to get some idea about the representativity of the sampling, it is appropriate to partition them into two different species: those that involve excitation of symmetric a_1 modes (ν_1 and ν_2) only, and those that involve excitation of two quanta of the optically inactive antisymmetric b_2 vibration (ν_3). States of the latter kind are not observed as such in the spectrum, but there is in principle a possibility that some of the peaks be split by Fermi resonance, although the splittings remain undetectable because of insufficient energy resolution. However, this kind of excitation by Fermi resonance is very weak in the present case. Only states (200), (210), and (300) could be perturbed [by states (002), (012), and (022), respectively] and their Franck–Condon factors are very small. We estimate the relative amount of these $(b_2)^2$ states to be at most 3×10^{-4} only with respect to the zero-order optically active states. Thus, the wave packet visits exclusively that part of the phase space which corresponds to the excitation of the totally symmetric modes ν_1 and ν_2.

On the other hand, the number $\mathcal{N}^*$ of *a priori* accessible phase-space cells has been estimated from Eq. (5.4) with $T^* = 5.4$ fs, and with the Franck–Condon factors determined by the three different laboratories.[37,55,56] One arrives at $\mathcal{N}^* = 6 \pm 1$.

This number $\mathcal{N}^*$ can also be partitioned according to measure $\xi^{(2)}$. It can be estimated that about 3% of the total number of states belong to the B_2 representation, whereas only about 0.7% results from the excitation of two quanta of the antisymmetric vibration. No further division by a factor of 3 is necessary in this case since the number $\mathcal{N}^*$ is too small for statistical considerations to apply.

In summary, what has been studied here is a weakly excited triatomic molecule. Relaxation is over after 2.4×10^{-14} s. The wave packet has then visited a fraction $\mathcal{F} \simeq (1.8 \pm 0.1)/(6 \pm 1) = 0.3 \pm 0.03$ of the total phase space compatible with the energy constraints. This ratio raises slightly to about 31% if the available phase space is restricted to totally symmetric states. The wave packet never accesses that part of the phase space that corresponds to the excitation of the antisymmetric vibration ν_3.

VII. THE $\tilde{X}^2B_3$ STATE OF $C_2H_4^+$

Several photoelectron spectra of the ground state of $C_2H_4^+$ are available.[35,45,54,57,58] That measured by Pollard *et*

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al.[35] is to be singled out for its excellent energy resolution. The smallest energy gap between two adjacent energy levels is of the order of 210 cm^{-1} which leads to a break time $\mathscr{T}_B \simeq (1.6 \pm 0.1)10^{-13}$ s. The corresponding autocorrelation function has also been determined up to time $\mathscr{T}_B$. Independent measurements have been carried out in the present laboratory[45] at a somewhat lower energy resolution. Results are given in Fig. 3.

The rate of propagation in phase space increases at first extremely rapidly. Starting from a value of zero, it reaches a maximum value of the order of 1.3×10^{14} cells s^{-1} at a time $T^* \simeq 1.35 \times 10^{-14}$ s (which corresponds to the first minimum of $|C(t)|$ for reasons explained in Sec. VI). The rate then decreases and is found to be reduced by a factor of 25 or more at the break time $\mathscr{T}_B$. At that same time, the effective number of cells which have been visited is indeed seen to reach its asymptotic value. A value of $\mathscr{N}_\infty = 10.7 \pm 1$ is determined in this way. The extrapolation formula (4.7) gives practically the same result (i.e., 10.6 ± 1).

From measurement of intensities [Eq. (3.8)], one deduces an estimate of $\mathscr{N}_\infty \simeq 8.2$ if each peak of the spectrum is treated as a particular Franck–Condon factor, i.e., if undetectable splittings are simply ignored. However, this value is a lower limit to $\mathscr{N}_\infty$ because optically active states can interact with neighboring inactive ones that belong to the totally symmetric representation. This brings about splittings which, although experimentally undetectable, should be accounted for in the calculation of $\mathscr{N}_\infty$ by Eq. (3.8). We have tried to estimate the occurrence of these interactions by generating the position of optically inactive states from a set of reasonable frequencies. Various assumptions have been considered. As expected, they all lead to an increase of the value of $\mathscr{N}_\infty$, but the results remain fortunately in the same range. The obtained value (9.5 ± 0.5) is in satisfactory agreement with that derived from the correlation function.

The measure $\xi^{(2)}$ of states involving an even number of quanta of antisymmetric vibrations [i.e., $(b_1)^2, (b_2)^2$, and $(b_3)^2$ states in the D_2 point group][59] is estimated to be weak: about one percent of the optically active states. Here again, phase space is not uniformly visited because the energy of the wave packet is too low to bring about excitation of antisymmetric vibrations.

How large is the available phase space? The envelope $S_T^*(E)$ has been calculated from Eqs. (5.2) and (5.3) with $T^* = 1.35 \times 10^{-14}$ s and is reproduced in Fig. 4. The summation (5.5) has been carried out exactly for the first 80 terms (up to an energy of 2170 cm^{-1}). At higher energies, it has been replaced by a numerical integration in which the density of states has been evaluated by the Beyer–Swinehardt[60] algorithm. The estimate of $\mathscr{N}^*$ obtained in this way is equal to $(2.0 \pm 0.7)\ 10^4$ cells. This value depends very sensitively on the exact shape of the high-energy wing of $S_T^*(E)$ because the density of states increases very rapidly with the internal energy.

The fraction of *a priori available* phase space is thus equal to $\mathscr{F} = \mathscr{N}_\infty / \mathscr{N}^* \simeq (5 \pm 2)10^{-4}$. However, the fractional occupation of the *effectively available* phase space is higher. Firstly, quantum restrictions discussed in Sec. V C reduce the number of accessible cells by a factor of 3. Secondly, the progression in phase space of the wave packet is in the present case restricted by strong selection rules. Only normal modes that belong to the totally symmetric representation can be optically excited. Hence, the quantum states that are really available necessarily belong to that representation.

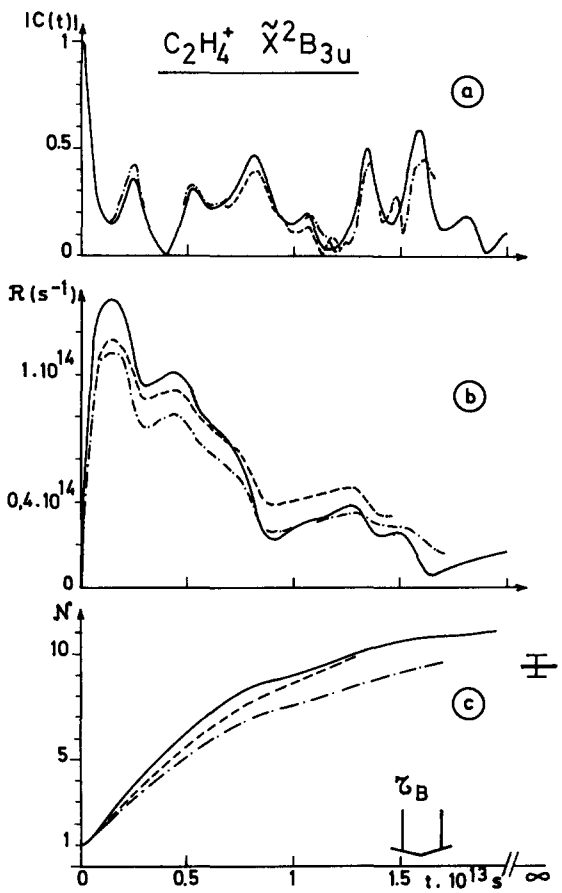

FIG. 3. (a) Autocorrelation function of state $\tilde{X}\ ^2B_3$ of $C_2H_4^+$. Solid line: results taken from Ref. 35. Dashed and dot-dashed lines: results taken from Ref. 45. (b) Rate of propagation in phase space (in s^{-1}). (c) Number of phase-space cells visited as a function of time. $\mathscr{T}_B$ = break time determined from Eq. (4.1). Extreme right: asymptotic value $\mathscr{N}_\infty$ determined from experimental Franck–Condon factors.

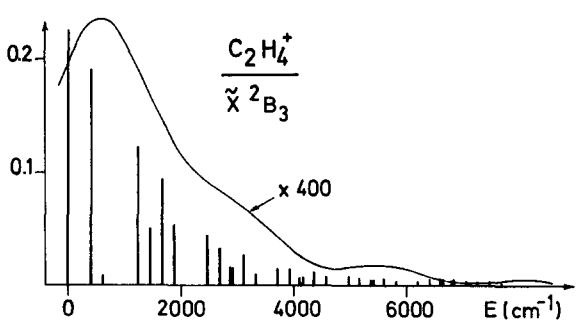

FIG. 4. Franck–Condon factors of state $\tilde{X}\ ^2B_3$ of $C_2H_4^+$. Stick spectrum: experimental factors p_k. The solid curve is the smoothed spectral function (envelope) $S_T^*(E)$ magnified by a factor of 400.

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Since the $C_2H_4^+$ ion is a hindered rotor,[35,59] classification can be made according to the D_2 point group which admits four irreducible representations (A,B_1,B_2, and B_3). As explained in Sec. V D, this reduces the number of available states by a further factor of 4. Altogether, this leads to a value of 12 for the reduction factor.

In summary, the dynamics involves approximately 0.05% of the *a priori* available phase space and 0.6% of the effectively available phase space.

VIII. PARTLY BOUND STATES

To shed some light on the kinetic problem, one should study the behavior of a high-energy wave packet, moving in an anharmonic potential close to the dissociation asymptote. We thus turn to a situation where the dissociation asymptote falls within the Franck–Condon region.

First of all, notice that the measure μ defined in Eq. (2.2) has to be used with care. Consider first a classical model in which the phase space is partitioned into two homogeneous cells: one having a volume V_1 and a density ρ_1, the second a volume V_2 and a density ρ_2. The probability of finding a particle in volume V_i is $n_i = \rho_i V_i$. Then, from Eqs. (2.2), (3.2), and (3.3),

$$\begin{aligned} h^{-f}\mu^{-1} = \mathrm{Tr}^{\mathrm{cl}}(\rho^2) &= \iint_{V_{\mathrm{tot}}} \rho^2 d\mathbf{p}\, d\mathbf{q} \\ &= \rho_1^2 V_1 + \rho_2^2 V_2 \\ &= n_1^2/V_1 + (1-n_1)^2/V_2. \end{aligned} \tag{8.1}$$

Thus, when the volume of one cell becomes very large (say $V_2 \to \infty$), the measure μ depends on the characteristics of the smaller cell only and is irrelevant to the dynamics in the larger cell. This situation naturally occurs in, e.g., predissociation when one part of the initial wave packet can be trapped in a bound potential whereas the other part explores the infinite phase space associated with a continuum. However, the ideas and methods described in the previous sections remain valid if one discards the unbound part and concentrates on the trapped component of the wave packet.

Divide the spectral function into two contributions:

$$S(E) = S_b(E) + S_u(E) \tag{8.2}$$

(index b stands for "bound," u for "unbound").

$$S_b(E) = \sum_n p_n \delta(E - E_n). \tag{8.3}$$

The normalization condition reads

$$\sum_n p_n + \int_{E_d}^{+\infty} S(E)dE = 1, \tag{8.4}$$

where E_d is the threshold of the continuum. Each part of the wave packet gives rise to its own correlation function, normalized to unity at time $t = 0$. Thus,

$$C_b(t) = \int_{-\infty}^{E_d} S_b(E) e^{-iEt/\hbar} dE \Big/ \int_{-\infty}^{E_d} S_b(E)dE \tag{8.5}$$

and a similar definition for $C_u(t)$. Then, substituting Eqs. (8.2) and (8.4) into Eq. (8.5), one has

$$C_b(t) = \left[C(t) - \left(1 - \sum_n p_n\right) C_u(t)\right] \Big/ \left(\sum_n p_n\right). \tag{8.6}$$

The desired quantity is the number of phase-space cells $\mathcal{N}_b$ occupied by the "bound part" of the DSE as a function of time:

$$\begin{aligned} \mathcal{N}_{b_T}^{-1} &= (2/T)\int_0^T (1 - t/T)\,|C_b(t)|^2 dt \\ &\simeq (2/T)\int_0^{T^*} (1 - t/T)\,|C_b(t)|^2 dt \\ &\quad + (2/T)\left(\sum_n p_n\right)^{-2} \int_{T^*}^T (1 - t/T)\,|C(t)|^2 dt, \end{aligned} \tag{8.7}$$

where T^* has the same significance as in Sec. IV and where it has been assumed that $C_u(t \geqslant T^*) \simeq 0$. To describe the behavior of the bound wave packet during the short period of time $[0, T^*]$, a crude expression is sufficient. We use Eq. (5.9) with $\omega T^* = \pi$. Then,

$$\begin{aligned} \mathcal{N}_{b_T}^{-1} \simeq \left(\sum_n p_n\right)^{-2} \Big[&\mathcal{N}_T - (2/T) \\ &\times \int_0^{T^*} (1 - t/T)\,|C(t)|^2 dt \Big] \\ &+ (1+\gamma)(T^*/T)(1 - T^*/2T) \\ &+ 2(1-\gamma)(\omega T)^{-2}. \end{aligned} \tag{8.8}$$

Hence,

$$\lim_{T\to\infty} \mathcal{N}_{b_T}^{-1} = \mathcal{N}_{b_\infty}^{-1} = \left(\sum_n p_n\right)^{-2} \mathcal{N}_\infty^{-1}. \tag{8.9}$$

The quantity $\mathcal{N}_\infty^{-1}$ can also be determined as follows. The initial wave packet is given by

$$|\varnothing(0)\rangle = \sum_k a_k e^{-iE_k t/\hbar} |k\rangle + \int dE\, a_E e^{-iEt/\hbar} |E\rangle, \tag{8.10}$$

where $|E\rangle$ denotes the wavefunctions of the Hamiltonian H of the system corresponding to the continuous spectrum. The correlation function now has the form

$$\langle \varnothing | \varnothing(t) \rangle = \sum_k p_k e^{-iE_k t/\hbar} + \int dE\, p_E e^{-iEt/\hbar} \tag{8.11}$$

with

$$p_E = |a_E|^2. \tag{8.12}$$

Using formulas (3.8) and (8.11), one immediately arrives at the following expression for $\mathcal{N}_\infty$:

$$\mathcal{N}_\infty^{-1} = \lim_{T\to\infty} (1/T)\int_0^T |\langle \varnothing | \varnothing(t) \rangle|^2 dt = \sum_k p_k^2 \tag{8.13}$$

Thus, in agreement with our intuition, only the Franck–Condon factors of the discrete part of the spectrum determine the asymptotic value of the quantum measure. There is no contribution from the continuum states. This has a simple physical meaning. The unbounded part of the wave packet goes away and cannot contribute to the recurrences of the correlation function, thus being irrelevant to the asymptotic value of the quantum measure defined in Sec. II. This result remains valid if two or more continua (resulting either from

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adiabatic dissociation asymptotes or from surface crossings with repulsive states) are present.

Substituting Eq. (8.13) into Eq. (8.9), one finds

$$\mathcal{N}_{b_\infty}^{-1} = \sum_k (\bar{p}_k)^2 \tag{8.14}$$

with

$$\bar{p}_k = p_k / \sum_n p_n. \tag{8.15}$$

The set $\{\bar{p}_k\}$ forms a set of renormalized Franck–Condon factors for the discrete part of the spectrum only. On the other hand, $\mathcal{N}_\infty$ has in the present case no physical significance, since it is the quantity $\mathcal{N}_{b_\infty}$ which represents the number of phase-space cells occupied by the DSE in the long-time limit.

IX. THE $\tilde{B}^2\Sigma^+$ STATE OF HCN^+

The third band in the photoelectron spectrum presents a very complicated appearance[33,61] (Fig. 5). Starting around 19 eV, it first consists of a series of about 15 peaks which are extremely irregular both with respect to energy spacings and intensities. That part of the spectrum is totally incompatible with the usual model of a set of loosely coupled harmonic oscillators. It is followed by a few diffuse peaks which soon merge into a continuum. Clearly, one has to isolate the extremely anharmonic motion of a bound wave packet within energy limits ranging approximately between 19 and 20 eV. Some indications concerning the potential energy surface have been obtained from *ab initio* calculations.[62,63] The existence of stable states is accounted for by a hump of the potential.[63] The continuum part of the spectrum starts above this hump. In addition, the surface is conically intersected by lower states,[62] but from the appearance of the spectrum, we assume that these crossings take place on the outer part of the hump. The correlation function of the entire band has been previously determined.[33] We have submitted it to the analysis of Sec. VIII. The necessary parameters have been chosen in the following ranges: $T^* = (1.3 \pm 0.2) \times 10^{-14}$, $\gamma = [0 - 0.005]$, $\Sigma_n p_n = [0.5\text{–}0.67]$.

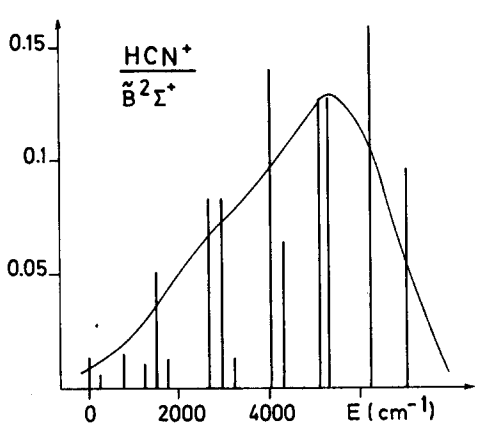

FIG. 5. Franck–Condon factors of state $\tilde{B}^2\Sigma^+$ of HCN^+. Stick spectrum: experimental factors p_k (followed in the experimental spectrum by a few diffuse peaks and by a continuum which are not represented here). The solid curve is the smoothed spectral function (envelope) $S_T^*(E)$.

For the break time, we estimate a value of $(2 \pm 0.4) \times 10^{-13}$ s. In the present case, the experimental determination of $C(t)$ is possible up to about $0.5\,\mathcal{T}_B$ only. However, it is possible to determine $\mathcal{N}_{b_\infty}$ by extrapolation [Eq. (4.7)]. The value obtained (17 ± 4) should be compared with that deduced from Franck–Condon factors. The latter are not easily measured. The set of values determined by Fridh and Åsbrink[61] lead to a value of 9.3 for $\mathcal{N}_\infty$ (more properly, $\mathcal{N}_{b_\infty}$). However, for reasons already discussed in the previous sections (failure to detect Fermi resonances), this value is certainly a lower limit. Reexamination of the spectrum determined by Delwiche *et al.*[33] suggests that a value of 10 (or more) would be more appropriate.

The number of available phase-space cells can be estimated in several ways. From Eq. (5.5), taking into account the uncertainty in the Franck–Condon factors, one arrives at $\mathcal{N}^* \simeq 13 \pm 2$. Equation (5.11) leads to $\mathcal{N}^* \simeq 9 \pm 4$, while a number $\mathcal{N}^* \simeq 14$ is compatible with Eq. (5.13).

Obviously, a better resolved spectrum would be desirable, but we infer from the data so far available that $\mathcal{N}_\infty$ and $\mathcal{N}^*$ have comparable magnitudes and therefore that the fraction $\mathcal{F}$ of occupied phase space is roughly equal to unity. No further division by a factor of 3 comes into play since the molecule is too small. Symmetry partitioning is irrelevant in such an irregular spectrum. In short, the phase space is completely visited in this case, in spite of the fact that the system has a discrete spectrum and cannot be chaotic.[64]

We thus conclude that the $\tilde{B}\ ^2\Sigma^+$ state of HCN^+ provides an example of "a system...(which is)...strongly but nonstochastically coupled, with the effect of a fluctuating set of Franck–Condon factors to states which have no simple zero-order assignment."[26] Also,[22] "contrary to what one might tend to believe, even two degrees of freedom (in the present case three) are sufficient to produce...a complex system with a classically chaotic counterpart."

X. DISCUSSION

Three cases of intramolecular vibrational energy relaxation of increasing complexity have been studied. In the ground state of H_2O^+, a low-energy wave packet undergoes low-amplitude vibrations in a nearly harmonic potential, so that its motion is severely restricted by selection rules. The exploration of the phase space ends after a break time $\mathcal{T}_B = 2.4 \times 10^{-14}$ s. At that moment, 30% of the phase space only has been visited. The sampling is biased in the sense that the density of states is too low and the anharmonicity too weak to allow Fermi resonances between zero-order states.

Comparison with the case of the ground state of $C_2H_4^+$ allows us to study the influence of the number of degrees of freedom. The time necessary to explore the phase space is now larger $[\mathcal{T}_B \simeq (16 \pm 1) \times 10^{-14}$ s$]$. The number of *a priori* accessible phase-space cells increases enormously and the fraction of occupied phase space is now as low as $(5 \pm 2) \times 10^{-4}$. This fraction raises to a value of about 6×10^{-3} if calculated with respect to the volume of phase

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space effectively available to the initial wave packet. As in the case of H_2O^+, Fermi resonances play a very minor role, because the density of states is again too low to allow energy transfer to antisymmetric zero-order modes.

The final example allows us to study the influence of a very strong anharmonicity in a small system. The potential energy surface of the $\tilde{B}\ ^2\Sigma^+$ state of HCN^+ is so complicated that the vibrational states cannot be classified in terms of a set of quantum numbers. The break time $[\mathscr{T}_B \simeq (20 \pm 4) \times 10^{-14}\ \text{s}]$ is much longer than that observed in the case of the other triatomic. To a good approximation, the phase space is fully visited.

The values obtained for $\mathscr{T}_B$ are much shorter than the pico- and nanosecond time scales commonly alluded to in the literature[6-10,15-18] on intramolecular vibrational energy relaxation. However, the values which have been obtained here refer to small systems at low energies. The break time $\mathscr{T}_B$ has been found to increase with the complexity of the molecules and with its internal energy.

What remains to be done (and this will be our aim in future papers of this series) is to look for spectroscopic data out of which information more directly related to chemical processes can be extracted. It would be desirable to move as much as feasible to higher internal energies for molecular systems larger than triatomics.

XI. CONCLUSIONS

In the assessment of the impact of the present results on the understanding of unimolecular dissociation, a number of points should be kept in mind.

(1) It is sometimes said that, since there is a mathematical equivalence between a spectrum and its autocorrelation function, no radically new information can be derived from the latter. This is not quite true. First, the original experimental information $S_{\text{exp}}(E)$ is upgraded to quantities with a more fundamental significance [i.e., $C(t)$ and $S(E)$] by a procedure which involves purification from experimental uncertainties and from the irrelevant rotational broadening and spin–orbit splitting. It has been seen that the method provides the easiest way to extract information from a poorly resolved spectrum. Secondly, whereas it is true that the quantities $\mathscr{T}_B, \mathscr{N}_\infty$, (and also $\mathscr{F}$ to a certain extent) are already contained in the optical spectrum, the analysis developed by Heller complements them with additional useful concepts (e.g., the rate $\mathscr{R}_T$ which cannot be easily extracted from the spectrum). Altogether, the use of the correlation function offers great advantages in giving a clear and attractive dynamical picture. The very fact that this information has been available all the time but remained unexploited till Heller developed a consistent scheme demonstrates the usefulness of the approach.

(2) Except in the case of HCN^+, the sampling of the phase space has been found to be biased by selection rules. The wave packet can only visit that part of Hilbert space made up of totally symmetric wave functions. However, in a zero-order representation in terms of normal modes, only antisymmetric modes are coupled to the continuum. The representativity of the sampling of phase space depends on the presence of strong vibrational couplings[52] (e.g., Fermi resonances) which lead to excitation of zero-order antisymmetric modes by an even number of quanta and thus allow the system to access parts of the phase space which would never be visited in a separable system. A high density of states in a strongly anharmonic potential (i.e., the situation which normally exists close to a dissociation asymptote) leads to nonseparability of the quantum vibrational wave functions and improves the representativity of the sampling of phase space. This is a necessary condition for the validity of the RRKM theory. Thus, one has an explanation to the rule according to which a low density of states leads to incomplete or slow intramolecular vibrational relaxation.[14-17]

(3) Statistical theories are based on consideration of a microcanonical ensemble (i.e., a well-defined energy), whereas the present method implies consideration of a wave packet. Therefore, the quantities derived from experiment ($\mathscr{T}_B$, $\mathscr{F}$, etc.) are really averages over a certain range of internal energies.

(4) It has been repeatedly stated in the literature on intramolecular dynamics[7,26,30,47] (but this point is unfortunately overlooked by many kineticists using RRKM theory), that the characteristics of intramolecular vibrational energy relaxation depend as much on the excitation process as on the nature of the molecule. Thus, no distinction should be drawn between "RRKM" and "non-RRKM molecules." Different excitation processes may lead to different initial wave packets, and a particular system may belong to either category depending on the way it has been energized.

An ideal experiment has been studied here: a pure Franck–Condon transition from a vibrationally cold ground state under collision-free conditions. This situation has to be considered as a particular probe implying a maximum number of restrictions, and the results are not necessarily valid for other experimental situations. If the initial preparation leads to a statistical mixture (instead of a pure quantum state as has been considered so far), a mixed-state density operator has to be used. This reduces the constraints, both those which result from symmetry considerations and those which concern the quantum ergodic χ^2 random fluctuations. This will be the case in a number of well-known experimental situations, e.g., an electronic transition involving hot bands, or taking place from several autoionizing states, or implying collisions in the preparation (e.g., charge transfer), or if the initial molecule is itself prepared from a preliminary dissociation, etc. Therefore, when less constraints are introduced in the preparation, the present results give in fact a lower limit to the fraction $\mathscr{F}$ of visited phase space.

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