Chaos and Dynamics on 0.5–300-ps Time Scales in Vibrationally Excited Acetylene: Fourier Transform of Stimulated-Emission Pumping Spectrum

J. P. Pique,[a] Y. Chen, R. W. Field, and J. L. Kinsey

Department of Chemistry and George Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 27 October 1986)

A recently proposed technique based on the Fourier transform of the spectrum is applied to the stimulated-emission pumping spectrum of acetylene at $\sim 26\,500$ cm^{-1} above the vibrational ground state. Correlations on two different time scales (~ 3 and ~ 45 ps) were found from analysis of low-resolution (0.3 cm^{-1}) and high-resolution (0.05 cm^{-1}) spectra, respectively. Additional structure produced dynamic information on a wider (0.5–300 ps) time scale. The results show that acetylene at 26 500 cm^{-1} is in the transition from the regular to the chaotic regime.

Molecular spectroscopy allows access to large numbers of energy levels, whose statistical properties are useful in testing theories of "quantum chaos."[1] Berry and Tabor have shown that a classically regular system gives eigenvalues randomly located with respect to each other in the semiclassical limit.[2] In a chaotic regime, however, adjacent eigenvalues repel each other to produce a more rigid spectrum.[3,4] This effect can be exhibited either in terms of short-range correlations (e.g., nearest-neighbor distributions) or longer-range correlations. Double-resonance spectroscopy, with its capability of presorting spectra, provides a particularly good experimental opportunity for the study of correlations among the locations of eigenstates. Until now there have been only two experiments showing rigidity in the statistics of level placement in a molecule: The first evidence came from a stimulated-emission pumping (SEP) spectrum of very high vibrational levels (at $\sim 27\,900$ cm^{-1}) of the ground electronic state of acetylene (C_2H_2)[5]; the second came from a singlet-triplet (S_1-T_1) anticrossing spectrum of methylglyoxal.[6]

Important questions are the spectroscopic signatures of a dynamically chaotic system and their implications with respect to the physical properties of the system. The pioneering work in this area was done by nuclear physicists, who proposed[7] a variety of indices for describing short- and long-range correlations in nuclear spectra obtained by low-energy neutron scattering. These include the nearest-neighbor distribution and the Σ^2 and Δ_3 functions. These diagnostics rely on a "stick" spectrum of the levels being analyzed. Such procedures are susceptible to error due to finite resolving power (which might fail to reveal small separations between adjacent levels) and a finite signal-to-noise ratio (which might cause weak features to be overlooked). Methods free of these difficulties are desirable.

A recently proposed new technique[6] based on the Fourier transform (FT) of the spectrum provides a partial solution to these problems. Because the FT shows long-range correlations among levels, it is relatively insensitive to resolution. The linearity of the FT also reduces sensitivity of the result to missed weak features. In this Letter, we apply this technique to show the existence of correlations on two different time scales (3 and 45 psec) in a very-high-quality SEP spectrum of acetylene at $\sim 26\,500$ cm^{-1} above the vibrational ground state. We propose a tentative model for this. These results substantiate the existence of and approximately locate the region of transition to chaos in the ground state of C_2H_2.

When a spectrum is produced by a double-resonance scheme as are the SEP spectra reported here, the power of the FT diagnostic lies in a very physical fact. In an SEP experiment[8] the "pump" laser prepares a well-behaved initial state $|\Psi\rangle$ in an electronically excited state. This state is projected as a coherent superposition (wave packet) of stationary eigenstates of the ground state by the "dump" laser (which dumps population into the target level):

$$|\Psi\rangle = \sum_n a_n |n\rangle \tag{1}$$

and

$$|\Psi(t)\rangle = \sum_n a_n e^{-iH_G t}|n\rangle, \tag{2}$$

where H_G is the ground-state Hamiltonian and $|n\rangle$ one of its eigenstates. According to Heller[9] and Pechukas,[4] the square of the modulus of the Fourier transform (SMFT) of the spectrum $I(\omega)$ directly gives the survival probability of the initial state, $P(t)$:

$$P(t) \equiv |\langle\Psi|\Psi(t)\rangle|^2 = |\int I(\omega)e^{-i\omega t}dt|^2. \tag{3}$$

This dynamic quantity can provide a test for chaos or regularity in experimental spectra, and it could also be useful for treating quantum or semiclassical model systems. A comparison between $P(t)$ as calculated above from $I(\omega)$ and as calculated from $|\Psi(t)\rangle$ obtained by (quantum or semiclassical) solution of the time-depend-

ent Schrödinger equation would be very instructive.

Spectral correlations appear naturally in the FT (denoted by $\mathcal{F}$) of the autocorrelation of the spectrum $I(\omega)$.[6,10] If the position, width, and intensity of a line are assumed to be statistically independent of each other, the following result is obtained for a set of levels which belong to the same symmetry species[6]:

$$\mathcal{F}[I(\omega)\otimes I(\omega)] = |\mathcal{F}I(\omega)|^2 = N^2 A_E^2(t)\langle y\rangle^2\langle L(t,\Gamma)\rangle^2 + N\langle y^2\rangle\langle L^2(t,\Gamma)\rangle[1 - G(t)b_2(t)]\otimes A_E^2(t). \tag{4}$$

N is the number of lines in the spectrum, $A_E(t)$ is the FT of the envelope of the portion of spectrum analyzed, $L(t,\Gamma)$ is the FT of the normalized line shape of individual lines (of width Γ), y is an integrated line intensity, and the brackets $\langle\ldots\rangle$ indicate an average over all the features contained in the spectrum analyzed. The first (fast) component is proportional at $t=0$ to the square of the number of lines and decays like the SMFT of the envelope A_E. The second (slow) component is proportional at $t=0$ to N and decays like the SMFT of the line shape L. The central quantity is b_2; this is the SMFT of the cluster function Y_2 introduced by Mehta,[11] which describes the strict second-order correlations between the locations of two levels. If the level positions are correlated, b_2 induces a "correlation hole" which appears just following the decay of the fast component. A mathematical analogy can be made between the correlations in energy among spectral lines and the spatial correlations of atoms in a liquid or solid. According to this analogy, the quantity $b_2(t)$ plays the role of the "structure factor" in light-scattering theory.[12] We expect b_2 to contain information about interaction matrix elements.[12]

$G(t)$ reflects the distributions in line intensity y and linewidth Γ. It is defined by

$$G(t) \equiv \langle y\rangle^2\langle L(t,\Gamma)\rangle^2/\langle y^2\rangle\langle L^2(t,\Gamma)\rangle. \tag{5}$$

For a Lorentzian line shape $G(t=0) = \langle y\rangle^2\langle\Gamma\rangle^2/\langle y^2\rangle\langle\Gamma^2\rangle$. $G(t)$ is related to Heller's F parameter.[9] Since $G \leq 1$, it attenuates the amplitude of the correlation hole. It is also interesting to note that the ratio between the fast component and the asymptotic value [when $b_2(t)=0$] of the slow component is NG. This allows a value of G to be extracted from the spectrum, provided that a value of N is obtained by a counting of the number of features in the spectrum.

The experimental results that we report here come from a very clean SEP spectrum of C_2H_2 which is composed of, at most, two sets of levels. The details will be presented in a forthcoming paper.[13] Briefly, with use of a $Q(1)$ pump transition, a single level of the $\tilde{A}\,^1A_u$ state was excited with $J'=1$, $K'=1$, and two quanta of vibration in the trans-bend mode (ν_3). The only possibilities for the dump transition are $Q(1)$ and $P(2)$ lines connected, respectively, to $l''=0$ and $l''=2$ levels of profoundly different vibrational character. The possible indeterminancy between an SEP (downward) or an upward transition has also been resolved definitively.[13]

Figure 1 shows a very short part of the large and high-quality SEP spectrum recorded between 25 850 and 27 250 cm^{-1}. In this energy region, a low-resolution (0.3 cm^{-1}) SEP spectrum of C_2H_2 is composed of broad features, "clumps,"[5] with a density ρ_c of $\sim 0.6/$cm^{-1} [Fig. 1(a)]. The high-resolution spectrum (0.05 cm^{-1}) [Fig. 1(b)] reveals the presence of a finer structure with a density ρ_f of $\sim 8/$cm^{-1}. The clump structure has the appearance of an intensity modulation of this dense set of lines. The fact that ρ_c and ρ_f are close, respectively, to the density of Franck-Condon "bright levels" and the total density of states of a given symmetry (calculated crudely by a direct count in an anharmonic-normal-mode picture) suggests that each clump corresponds to one of the bright levels, i.e., to a zero-order promoting basis function carrying oscillator strength. The fine structure corresponds to the mixing of the much more numerous basis functions corresponding to dark levels into the sin-
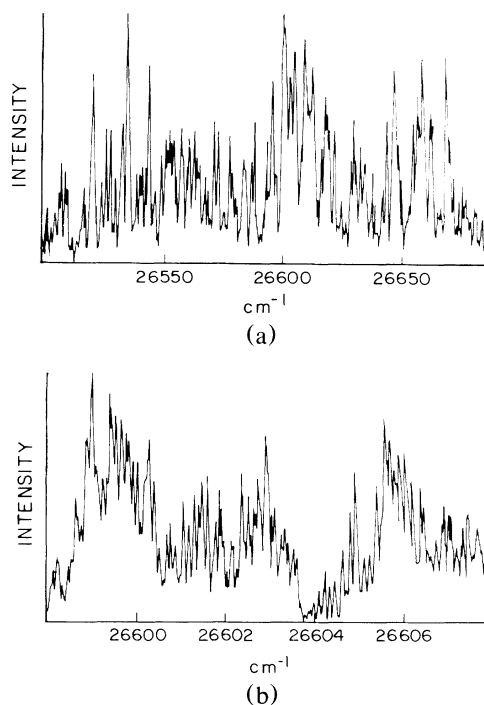

FIG. 1. (a) Part of a low-resolution (0.3 cm^{-1}) C_2H_2 SEP spectrum at 25 850–27 250 cm^{-1} of vibrational energy in the ground electronic state ($\tilde{X}\,^1\Sigma_g^+$). The density of "clumps" is $\sim 0.6/$cm^{-1}, resulting in ~ 850 recorded clumps. (b) Part of a high-resolution (0.05 cm^{-1}) C_2H_2 SEP spectrum. The long-range modulation in intensity is due to the clump structure. The density of lines is $\sim 8/$cm^{-1}.

gle bright level, as in the theory of "radiationless transitions."[10]

The SMFT of the spectrum is reported in Fig. 2. To generalize Eq. (4) we used an analogy with the theory of light scattering[12] for a two-component mixture and defined three structure factors: b_2^c, b_2^f, b_2^{cf} corresponding, respectively, to clump-clump and fine-structure–fine-structure correlations, and an interference term between the two structures. This interference term can be a major problem for the interpretation of light-scattering experiments. However, it is easy to cancel its effect in our case because we performed the experiment in direct energy space. Effectively, measurements at low-resolution cancel the fine structure and consequently the interference term. Alternatively, FT of a part of the spectrum with a small number of clumps cancels the effect of b_2^c and b_2^{cf}. Thus b_2^f and b_2^c may be separately determined, free of contamination by b_2^{cf}. Averaging the FT of several individual clumps improves the statistics.

The important result is shown in Figs. 2(a) and 2(b), which show "correlation holes" corresponding to the clump structure and fine structure. The correlation
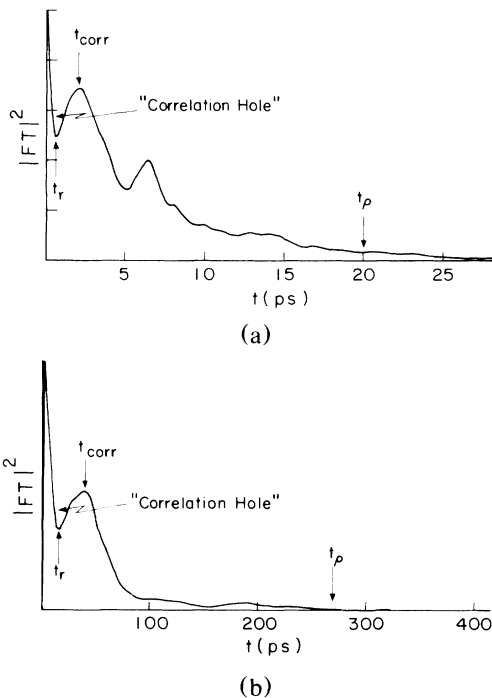

(a)

(b)

FIG. 2. (a) Slow component of the smoothed SMFT of the clump spectrum from 25 850 to 27 250 cm^{-1}. The value of t_r gives $\omega_{range} \sim 60$ cm^{-1} for the correlation in the positions of the centers of clumps. The value of t_{corr} is $\sim \frac{1}{6} t_p$, where $t_p = \rho_c/c$. t_{corr}/t_p is a measure of the chaotic fraction of phase space (see text). (b) Slow component of the averaged SMFT of several parts of the high-resolution spectrum. The value of t_r gives $\omega_{range} \sim 3$ cm^{-1}. The value of t_{corr} is $\sim \frac{1}{6} t_p$, where $t_p = \rho_f/c$.

recovery times t_{corr} are well separated ($t_{corr} \sim 3$ psec for the clump and $t_{corr} \sim 45$ psec for the fine structure). There is a close similarity between those two FT and the diffraction picture of an amorphous solid.[12] After the characteristic correlation hole, systematic recurrences appear. These remain stable when we take the Fourier transform of different parts of the spectrum (provided that the segments are not taken to be too short). The first term in Eq. (4) contributes a maximum proportional to N^2 at the time origin, which decays in time because of the finite length of spectrum analyzed. This decay occurs within the first few channels of the FT spectrum and cannot be discerned in Fig. 2. At a longer time, inside the correlation hole, there is a minimum whose location t_r gives a measure of the interaction range of the level correlations:

$$\omega_{range} = (ct_r)^{-1}. \tag{6}$$

$\omega_{range} \sim 60$ cm^{-1} for the clump structure, and $\omega_{range} \sim 3$ cm^{-1} for the fine structure.

The initial recovery from the correlation hole does not occur at $t_{corr} = t_p$, as for a Gaussian orthogonal ensemble or Wigner distribution,[6] but at $\sim \frac{1}{6} t_p$ ($t_p = \rho/c$, where $\rho = \rho_c$ or ρ_f). A hole with $t_{corr} = t_p$ would indicate the absence of any good quantum numbers except energy, angular momentum, and parity. A hole with $t_{corr} < t_p$ suggests the presence of several (~ 6) "symmetry species" of some additional good or approximately good quantum numbers. Thus, the experimental results show that $\sim 26\,500$ cm^{-1} is an intermediate energy, within the transition from the regular regime to the chaotic one. The FT of spectra near 27 900 cm^{-1} suggests fully chaotic dynamics at only ~ 1400 cm^{-1} higher energy. The position of the rebound from the correlation is a direct measure of the chaotic fraction of phase space. Taking into account the fact that we may have access to two sets of levels [$Q(1)$ and $P(2)$ lines] the fraction of phase space calculated from our spectra is about 34%.

The existence of correlations in both clump and fine-structure spectra allows us to postulate that the Hamiltonian of the system may be written as

$$H = H_0 + V' + V''. \tag{7}$$

The observation of bright levels shows the existence of a good basis for the zero-order Hamiltonian. In our model, V' mixes the bright levels among themselves and V'' mixes bright and dark levels. The strengths of $\rho_c \langle V'^2 \rangle$ and $\rho_f \langle V''^2 \rangle$ are such that the clump and the fine structures are both "chaotic." Because the ratio ρ_c/ρ_f is about 0.08, V' must be much larger than V''. V' could be something like the lowest-order terms of a Fermi interaction and V'' the higher-order terms. Because of the complexity of the spectrum, we are not presently able to ascertain the nature of V' and V''. However, we are trying to extract some information about the moments of V' and V'' from the shape of the FT. Such a measure will

provide a very interesting connection with a calculation on the correlation properties of eigenvalues of a random matrix, which predicts that the nearest-neighbor distribution is governed by the mean value of the modulus of off-diagonal elements.[14]

Instead of characterizing the degree of chaos with a single number, we have shown that the FT technique provides a real dynamic diagnostic with multiple information. We are able to access times in the range 0.5–300 psec. The only limits are the length of the spectrum undergoing FT analysis on the one hand, and the resolution of the lasers and the density of lines in the spectrum on the other. The existence of correlations at two time scales and the discovery of the position of the transition to chaos in the ground state of C_2H_2 are of fundamental interest and lead us to believe that C_2H_2 will provide the most complete and detailed information about quantum chaos in a real molecular system.

(a)Permanent address: Laboratoire de Spectrometrie Physique, Université Scientifique et Médicale de Grenoble, BP 87, 38402 Saint Martin d'Heres Cédex, France.

[1]D. W. Noid, M. L. Koszykowski, and R. Marcus, Ann. Rev. Phys. Chem. 32, 267 (1981); E. J. Heller and R. L. Sundberg, in Proceedings of the NATO Advanced Research Workshop on Chaotic Behavior in Quantum Systems, edited by G. Casati (Plenum, New York, 1985).

[2]M. V. Berry and M. Tabor, Proc. Roy. Soc. London, Ser. A 306, 375 (1977).

[3]E. P. Wigner, SIAM (Soc. Ind. Appl. Math.) 9, 1 (1967).

[4]P. Pechukas, Phys. Rev. Lett. 51, 943 (1983).

[5]E. Abramson, R. W. Field, D. Imre, K. K. Innes, and J. L. Kinsey, J. Chem. Phys. 80, 2298 (1986).

[6]L. Leviandier, M. Lombardi, R. Jost, and J. P. Pique, Phys. Rev. Lett. 56, 2449 (1986).

[7]T. A. Brody, J. Flores, J. B. French, D. A. Mello, A. Pandey, and S. S. Wong, Rev. Mod. Phys. 53, 385 (1981); O. Bohigas, M. J. Gionnoni, and C. Schmit, Phys. Rev. Lett. 52, 1 (1984).

[8]C. Kittrell, E. Abramson, J. L. Kinsey, S. A. McDonald, D. E. Reisner, R. W. Field, and D. H. Katayama, J. Chem. Phys. 75, 2056 (1981); D. E. Reisner, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys. 80, 5968 (1984).

[9]E. J. Heller and R. L. Sundberg, in Proceedings of the NATO Advanced Research Workshop on Chaotic Behavior in Quantum Systems, edited by G. Casati (Plenum, New York, 1985), p. 255.

[10]J. M. Delory and C. Tric, Chem. Phys. 3, 54 (1974).

[11]M. L. Mehta, Random Matrices (Academic, New York, 1967).

[12]A. Guinier, X-Ray Diffraction (Freeman, San Francisco, 1963); D. A. McQuarrie, Statistical Mechanics (Harper & Row, New York, 1973).

[13]J. P. Pique, Y. Chen, R. W. Field, and J. L. Kinsey, to be published.

[14]R. Jost, in Proceedings of the Second International Conference on Quantum Chaos and Fourth International Colloquium on Statistical Nuclear Physics, Cuernavaca, Mexico, 1986, edited by T. H. Seligman, Springer Lecture Notes in Physics (Springer-Verlag, New York, to be published).