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DIRECT OBSERVATION OF NONCHAOTIC MULTILEVEL VIBRATIONAL ENERGY FLOW IN ISOLATED POLYATOMIC MOLECULES

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Direct Observation of Nonchaotic Multilevel Vibrational Energy Flow In Isolated Polyatomic Molecules

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With picosecond spectroscopy and molecular beams it is shown that nonchaotic *multilevel* vibrational energy flow is present in large polyatomic molecules. This Letter reports on this novel observation and its probing of the fundamental process of energy redistribution in molecules.

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The fundamental process of collisionless intramolecular vibrational energy redistribution (IVR) in polyatomic molecules has been extensively studied for at least two major reasons. Firstly, IVR plays a central role in a wide variety of molecular processes such as multiphoton dissociation, laser-selective chemistry, radiationless transitions, and unimolecular reactions.[1] Secondly, classical and semiclassical treatments[2] of vibrational dynamics in a coupled two-mode system (Henon-Heiles Hamiltonian) have revealed interesting changes in vibrational motion (quasiperiodic or chaotic) which depend on total energy and coupling parameters. The results have stimulated research aimed at defining and discovering analogous quantum behavior in molecules. For these reasons two fundamental questions concerning IVR in real molecules are important: Given the impulsive excitation of an isolated molecule to some nonstationary excited state, *how rapidly* does this initial state evolve to encompass other vibrational motions, and *to what extent* do other vibrational motions become involved in the vibrational motion as a whole?

An intuitive feel for the concept of IVR can be gained by consideration of the classical case of coupled oscillators represented in Fig. 1. With pendulum a initially set in motion and pendulum b at rest, the effect of the coupling V_{ab} is to transfer energy from a to b. In the quantum analog to this situation (Fig. 1, middle) a harmonic oscillator zero-order state $|a\rangle$ is assumed to be prepared by a light pulse at $t=0$. Due to the coupling V_{ab} to the zero-order state $|b\rangle$ (via anharmonicity, for instance) this initially prepared state evolves in time to contain some contribution from $|b\rangle$. It is this wave-function evolution which describes the flow of energy from the vibrational motion represented by $|a\rangle$ to that represented by $|b\rangle$. In the situation where the initially prepared $|a\rangle$ is coupled to more than one other level (Fig. 1, bottom) multilevel IVR occurs.

Time-integrated experimental measurements[3] concerning IVR are somewhat indirect in that the observables measured depend on IVR but are removed from the primary process itself. Recently, however, the combination of ultracold, seeded supersonic molecular beams with picosecond laser spectroscopy has been shown to be useful to the study in real time of a number of aspects of isolated-molecule dynamics.[4] In this Letter we report on the direct observation, using these techniques, of nonchaotic *multilevel* IVR in the large molecule, anthracene.

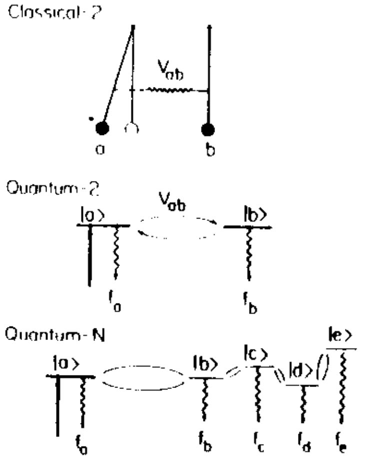

FIG. 1. Schematic representations of coupled oscillators in classical and quantum systems. In the quantum cases the probing of IVR by fluorescence spectroscopy is indicated. Note that other coupling schemes for quantum N are also possible.

We shall be concerned with IVR in anthracene at $\sim 1400\text{-cm}^{-1}$ excess vibrational energy in the first excited singlet electronic state S_1. At these energies the density of S_1 vibrational states is $\sim 25/\text{cm}^{-1}$. Excitation to S_1 from an S_0 level selectively prepares the (ultracold) molecule in one well-defined vibrational state (harmonic state) while the remainder of the states are not excited because of symmetry and/or Franck-Condon restrictions. The scheme of our experiment (Fig. 1) is to prepare such a well-defined optically allowed vibrational state, $|a\rangle$, and then to probe the temporal evolution of the state by temporally and spectrally resolving the fluorescence from the sample. In what follows, we shall show that the flow of vibrational energy from an initially prepared state to other vibrational states is manifested in fluorescence decays as modulations (quantum beats), the *phases* of which are spectrally dependent, and the number of Fourier components of which are dependent on the number of levels involved in the energy flow.

Consider the case of N coupled vibrational levels (Fig. 1, bottom). It is convenient to initially deal with the molecular eigenstates, $|I\rangle$, $I = 1,N$, which result from the coupling of these levels:

$$|I\rangle = \sum_{\gamma = a,b,c,\ldots} \alpha_{I\gamma}|\gamma\rangle, \tag{1}$$

where the α's are elements of a real orthogonal matrix.

Delta function excitation of a molecule from the vibrational level $|g\rangle$ of S_0 will prepare these N eigenstates coherently, given that at least one of the zero-order states $|\gamma\rangle$ has a nonzero transition moment with $|g\rangle$. The wavelength-integrated fluorescence versus time to the manifold of S_0 vibrational levels $\{|f\rangle\}$ is given by[5,6]

$$I(t) = C\sum_{f}\sum_{I,J=1}^{N} \mu(I,g)\mu(g,J)\mu(J,f) \times \mu(f,I)e^{-t(i\omega_{IJ}+\Gamma)}, \tag{2}$$

where C is a constant, the $\mu(I,g)$'s are dipole matrix elements between $\langle I|$ and $|g\rangle$, Γ is the excited-state decay rate (taken for simplicity to be the same for all N excited states), and $\omega_{IJ} = (E_J - E_I)/\hbar$, E_I and E_J being the energies of the eigenstates $|I\rangle$ and $|J\rangle$, respectively. Now, as noted above, usually only one harmonic vibrational level, say $|a\rangle$, within a given small energy region has nonzero absorption from $|g\rangle$. Thus, $\mu(I,g) = \alpha_{Ia}\mu(a,g)$ for all I. Similarly, for fluorescence into state $|f_\gamma\rangle$, $\mu(I,f_\gamma) = \alpha_{I\gamma}\mu(\gamma,f_\gamma)$ for all I. We shall call the corresponding fluorescence band a γ-type band. Given this it is clear from Eq. (2) that the fluorescence spectrum from an N-level system may contain as many as N types of bands, all with different temporal behaviors determined by the zero-order level which contributes to the emission dipole of the band. Furthermore, since the excited state formed by δ-function excitation is

$$\psi(t) = \sum_{I=1}^{N}\alpha_{Ia}|I\rangle\exp[-t(iE_I + \Gamma/2)],$$

it is clear with use of Eqs. (1) and (2) [restricting f to f_γ] that the intensity of a γ-type band, which is proportional to

$$\sum_{I,J=1}^{N}\alpha_{Ia}\alpha_{Ja}\alpha_{I\gamma}\alpha_{J\gamma}\exp[-t(i\omega_{IJ}+\Gamma)],$$

is also directly proportional to the contribution of $|\gamma\rangle$ to the excited state: $|\langle\gamma|\psi(t)\rangle|^2$. *Thus the measurement of the decays of different band types provides a direct picture of the vibrational content of the excited state.* In addition, being that the $|\langle\gamma|\psi(t)\rangle|^2$ are measures of vibrational chaos,[7] the fluorescence decays are related to this, too, as we shall discuss later.

The simplest case is for $N = 2$. Here, two types of bands can arise, a type and b type.[6] The temporal characteristics of each of the bands can be derived from Eq. (2) by using the eigenstate results for two-level coupling: $|1\rangle = \alpha|a\rangle + \beta|b\rangle$ and $|2\rangle = -\beta|a\rangle + \alpha|b\rangle$. Both types of bands have have fluorescence decays modulated by a $\cos\omega_{12}t$ interference term. However, the cosine term has a *negative* coefficient for the b-type band, whereas for the a-type band is it *positive*. These phase-shifted beats are manifestations of the oscillatory flow of energy between the $|a\rangle$ and $|b\rangle$ vibrational motions. (Note the analogy with the oscillatory distribution of energy that occurs in the coupled pendulums of Fig. 1.)

The spectral dependence of quantum beat phases also applies to $N \geq 3$. Herein, we only consider results for $N = 3$. In this case, a-, b-, and c-type bands can arise in the fluorescence spectrum. As is evident from Eq. (2) all three types will have decays modulated at the frequencies ω_{12}, ω_{23}, and $\omega_{12}+\omega_{23}$. The three cosine terms, however, will have different phases depending on the band type. In particular, it can be shown, with use of the orthonormal properties of the α's, that (1) for a-type bands all cosine terms are positive, (2) for b- and c-type bands two of the terms are negative and the third positive, and (3) the cosine term that is positive for the b-type band is different from that for the c-type band. The experiments reported here show that behavior matching these predictions occurs.

Our experimental apparatus is described in detail elsewhere.[4,8] Briefly, an anthracene beam is formed by expanding anthracene vapor at 180 °C with 35–50-psi helium through a 100-μm pinhole into a chamber at $< 10^{-3}$ Torr. A picosecond uv pulse ($\Delta t \sim 15$ ps, $\Delta\bar{\nu} \leq 2$ cm^{-1}) derived from frequency doubling a synchronously pumped, cavity-dumped (4 MHz) dye laser intersects the expansion 3 mm downstream from the pinhole. Fluorescence is collected with right-angle geometry, wavelength analyzed by a 0.5-m monochromator and detected by a fast multichannel plate photomultiplier (Hamamatsu R1564U). Decays are measured with time-correlated single-photon counting. Unlike our previous measurements,[4] the total time response of the detection system is now ~ 80 ps full width at half maximum. Decays are fitted by a single exponential function which is then subtracted from the data to yield the modulated portion (residual) of a given decay. One can analyze the residual for beat frequencies and phases by Fourier transformation of the residual, followed by division by the Fourier transform of the system response function. This automatically establishes the proper phases for the various beat components. Thus, positive cosine components appear as positive peaks in the real part of the Fourier transform and negative cosine ones as negative peaks.

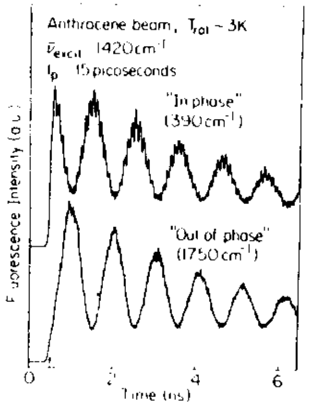

FIG. 2. The fluorescence decays of two bands in the spectrum of jet-cooled anthracene excited to $E_{vib} = 1420$ cm^{-1}. The arrow marks the temporal position of the excitation pulse.

A clear illustration of the concept of the spectral dependence of quantum beat phases is presented in Fig. 2, which consists of two decays taken for vibrational excitation of anthracene to 1420 cm^{-1} in S_1. The upper decay corresponds to detection of the fluorescence band at a red shift of 390 cm^{-1} from the excitation energy, and the lower decay to detection of the band at 1750 cm^{-1}. The slow modulation (~ 1 GHz) is clearly a positive cosine in the upper decay and a negative cosine in the lower decay. Two other prominent beat frequencies at 9.7 and 10.7 GHz also modulate the decays of Fig. 2. Fourier analysis reveals that all three beat components have 0° phases in the upper decay (a type), whereas in the lower decay (not a type) the 1- and 9.7-GHz components have 180° phases, and the 10.7-GHz components a 0° phase. Moreover, a third type of band has been observed, the decay of which has the 1-GHz component with 0° phase and the two fast components with 180° phases. The quantum beat behavior for this excitation therefore matches that expected for three coupled vibrational levels.

Another anthracene S_1 vibrational level which manifests multilevel coupling through spectrally dependent quantum beat phases is that which is populated by excitation to $E_{vib} = 1380$ cm^{-1}. Figure 3 displays the Fourier transforms of beat patterns for three of the bands that appear prominently in the fluorescence spectrum resulting from this excitation. The phases of the three beat components (3.5, 4.9, and 8.4 GHz) clearly match the predic-

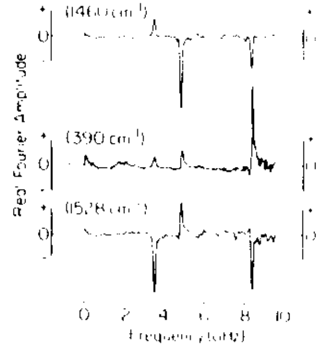

FIG. 3. Fourier-transform spectra of the quantum beat residuals of three bands in the fluorescence spectrum of anthracene excited to $E_{vib} = 1380$ cm^{-1}.

(4)

tions for three coupled vibrational levels.

Having directly observed vibrational energy flow in anthracene it is pertinent for one to consider the implications of these results. Firstly, it is evident that for excitations to $E_{vib} \cong 1400$ cm^{-1}, vibrational couplings from 1 to 10 GHz (~ 0.3 cm^{-1}) figure prominently in IVR processes. Secondly, it is meaningful that at these energies, energy flow involves approximately three levels spaced within 10 GHz. From direct counts of S_1 vibrational levels using calculated frequencies one would expect approximately ten levels in a 10-GHz region at $E_{vib} - 1400$ cm^{-1}. This implies selectivity in the extent of IVR for these levels.[9] Such selectivity could reasonably be the result of symmetry restrictions on vibrational coupling. Thirdly, the quantity $|\langle a|\psi(t)\rangle|^2$ has been shown[7] to be a useful measure of vibrational chaos in the quantum regime. Regular, periodic variations in this quantity indicate nonchaotic behavior. In this sense, then, the herein reported a-type decays, which are regular and periodic, represent the observation of nonchaotic IVR. Having demonstrated a technique for probing molecular states that are the quantum analogs of quasiperiodic regular motion we shall, in a future publication, show how the observation of rapid decay describes the analog of irregular motion and the rapid spreading out of energy deposited in a local region.[10]

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[1] See, e.g., N. Bloembergen and E. Yablonovitch, Phys. Today 31 (5), 23 (1978); A. H. Zewail, Phys. Today 33 (11), 27 (1980).

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[6] P. M. Felker and A. H. Zewail, Chem. Phys. Lett. 102, 113 (1983); the lack of influence of laser and detection polarizations on beats is discussed in this reference.

[7] M. D. Feit and J. A. Fleck, Jr., J. Chem. Phys. 80, 2578 (1984), and references therein.

[8] W. R. Lambert, P. M. Felker, and A. H. Zewail, to be published.

[9] Here, we have not considered the role of rotations in vibrational coupling. Experimental results to be published elsewhere show that the effect of rotations on modulated decays is primarily to enhance the rate of decay of quantum beat envelopes.

[10] For theoretical discussion see, e.g., G. Hose and H. S. Taylor, J. Chem. Phys. 84, 375 (1984).

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