

FIG. 2. A mass spectrum and energy distribution of He and D_2 .

of $\sim \pm 1.25$ ns. The time difference can be used to calculate the energy difference of the two ions according to their masses. The gases of our choice are He and D_2 . Their masses differ by 0.0256 amu and their ionization energies differ by 9.0 eV.

Figure 2 shows a mass spectrum of He^+ and D_2^+ taken at $V_{dc} = 4000$ V from the W (110) lattice steps, and also of D_2^+ at $V_{dc} = 3990$ V. This is the first time the He- D_2 doublet has been successfully resolved in the time-of-flight atom probe. The data also show the following features. (1) From their masses we find that at the same V_{dc} , the most energetic D_2^+ ions (indicated by

arrow B) have an energy 10 ± 1.05 eV larger than the He^+ ions (arrow A). (2) The most energetic D_2^+ ions at $V_{dc} = 3990$ V (arrow C) have, within ± 1.05 eV, the same energy as He^+ ions at $V_{dc} = 4000$ V. If the D_2^+ and He^+ ions are formed at the surface, then they should have the same energy of $\sim eV_{dc}$. If these ions are formed at their respective ionization zones, the D_2^+ should have an energy 9 eV larger than the He^+ . Our result agrees with the latter. Field desorbed gas ions always exhibit small but persistent low energy tails. Resonant peaks are often visible. This is exactly what has been observed in field ionization.² This feature thus further supports the thermal desorption-field ionization mechanism of pulsed-laser field desorption of gas molecules. In field evaporation of metals, ions are formed at the surface, and no persistent low energy tails have been observed.

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Semiclassical calculation of electronic spectra of supercooled anharmonic molecules

Arieh Warshel

Department of Chemistry, University of Southern California, Los Angeles, California 90007

Peter S. Stern

Chemical Physics Department, Weizmann Institute of Science, Rehovot, Israel 76100

Shaul Mukamel

Department of Chemistry, University of Rochester, Rochester, New York 14627

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We report here the calculation of the electronic absorption spectrum of supercooled methyl benzene using classical trajectories which are propagated on a realistic anharmonic potential surface. The method involves the classical calculation of the time dependent potential

energy gap $U(\tau)$ between the ground ($|a\rangle$) and excited ($|b\rangle$) electronic states, i. e., $U \equiv V_b - V_a$, V_i being the potential energy surface for the i th state. The spectrum is then obtained from $U(\tau)$ using two alternative approaches: The first approach uses the following expres-

sion for the spectrum¹:

$$I(\Delta) = \text{Re} \int_0^\infty d\tau \exp[-i\Delta\tau - g(\tau)], \quad (1)$$

where $\Delta \equiv \omega_L - \omega_{ba}$ is the detuning of the radiation frequency (ω_L) from the molecular electronic transition (ω_{ba}), and

$$g(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \langle U(0)U(\tau_2) \rangle \\ = - \sum_j 2 \left| \frac{A_j}{\omega_j} \right|^2 \{ \kappa_j [\exp(i\omega_j\tau) - i\omega_j\tau - 1] \\ + (1 - \kappa_j) [\exp(-i\omega_j\tau) + i\omega_j\tau - 1] \}. \quad (2)$$

Here A_j are the Fourier components of $U(\tau)$,

$$U(\tau) = \sum_j A_j \exp(i\omega_j\tau) \quad (3)$$

and

$$\kappa_j = \frac{1}{1 + \exp(-\omega_j/kT)}, \quad (4)$$

classically $\kappa_j = 1/2$. The fluctuation dissipation theorem was used in Eq. (2) to construct the quantum correlation function $\langle U(0)U(\tau) \rangle$. Our first procedure for the calculation of $I(\Delta)$ thus consists of running a long classical trajectory on the V_a potential surface from which we get $U(\tau)$, A_j , $g(\tau)$, and $I(\Delta)$. In principle, we should average g over an ensemble of trajectories in order to sample properly the initial phase space distribution but in many cases it is sufficient to consider one long trajectory instead.² In the special case where V_a and V_b are linearly displaced harmonic surfaces then Eqs. (1) and (2) yield the exact quantum-mechanical spectrum.¹ In this case, the j summation runs simply over the molecular normal modes. However, for a general anharmonic molecule, Eq. (2) is approximate [$g(\tau)$ is calculated only to second order in U which corresponds to a second order cumulant expansion]. In addition, the j summation will be, in general, infinite and any frequency may appear in the Fourier decomposition of $U(\tau)$ [Eq. (3)]. The second approach evaluates the spectrum using the direct semiclassical trajectory approach for surface hopping between the ground and the electronically excited states which are coupled by the tran-

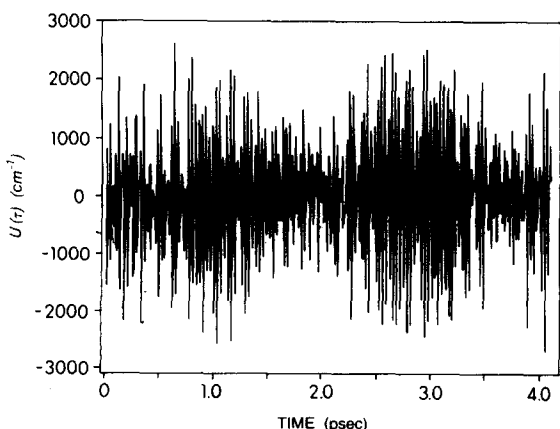


FIG. 1. The energy gap $U(\tau)$ for methyl benzene at $T = 0$.

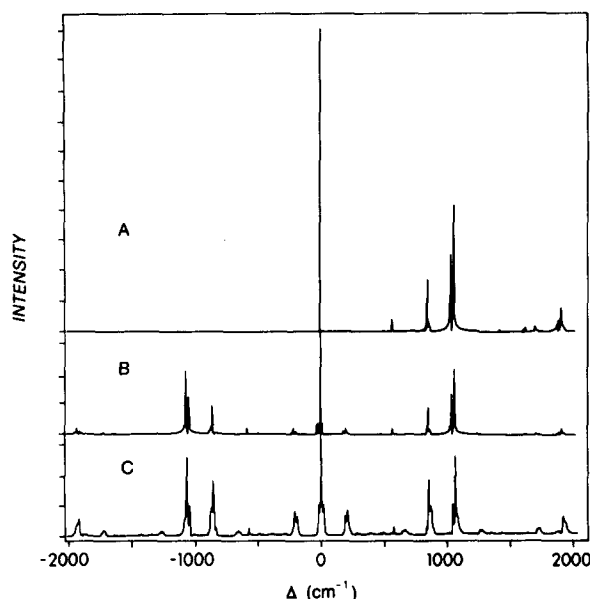


FIG. 2. The absorption spectrum of methyl benzene calculated using $U(\tau)$ of Fig. 1. (A) Quantum calculation using the fluctuation dissipation theorem [Eqs. (1) and (2) with $\kappa_j = 1$]. (B) Same as (A) but without invoking the fluctuation dissipation theorem ($\kappa_j = 0.5$). (C) Classical calculation [Eq. (5)]. The three spectra were normalized to have the same intensity of the fundamental 0-0 band.

sition dipole operator.^{3,4} This gives

$$I(\Delta) = \lim_{t \rightarrow \infty} \frac{1}{2t} \left| \int_0^t d\tau \exp \left[-i \sum_j \frac{A_j}{\omega_j} \exp(i\omega_j \cdot \tau) - i\Delta\tau \right] \right|^2. \quad (5)$$

In contrast to Eq. (2), Eq. (5) is nonperturbative in U but it does not render itself so easily to generate the corresponding quantum mechanical spectrum without a semiclassical quantization that involves a multidimensional solution to the Stueckelberg problem. At low temperatures $kT \ll \hbar\omega_j$, when quantum effects are significant we should therefore prefer Eq. (1) together with Eq. (2) to Eq. (5).

We have applied this procedure towards the calculation of the zero temperature absorption spectrum of methyl benzene which was studied experimentally in a supersonic beam.⁵ The OCF/PI program⁶ was used to calculate the ground and the excited (B_2) anharmonic potential surfaces. We then ran a classical trajectory in which each normal mode was initially in its equilibrium position with the zero point kinetic energy. The trajectory was calculated for 4 ps with an integration step of 10^{-4} ps and a standard fast Fourier transform routine was used to calculate A_j and the spectra. Figure 1 shows the energy gap $U(\tau)$ and Fig. 2 gives the absorption spectrum $I(\Delta)$ for methyl benzene at zero temperature calculated from $U(\tau)$ using three algorithms: (A) Is the quantum procedure [Eqs. (1) and (2) with $\kappa_j = 1$]. (B) Is the same procedure but without utilizing the fluctuation dissipation theorem ($\kappa_j = 1/2$), and (C) is the semiclassical calculation [Eq. (5)]. We note that (B) and (C) are symmetric [$I(-\Delta) = I(\Delta)$], as they should be in the *high temperature limit* and only in

(A) $I(-\Delta) = 0$ as the zero temperature spectrum should be. Moreover, (B) and (C) contain hot combination bands (e.g., the 200 cm^{-1} features) which should not exist at zero temperature. These are totally suppressed in (A). Procedure (A) thus seems most adequate towards the calculation of nonlinear spectra of large ultracold polyatomic molecules. The present method deliberately avoids the calculation of the time-dependent vibrational wave function which forms the basis for another semiclassical method developed recently.⁷ The wave function contains too much information than is actually needed for the calculation of the spectrum and its evaluation requires a much larger computational effort than made here, and may dictate some unnecessary approximations. Our method focuses directly on the spectrum, as is done in macroscopic theories of line broadening.⁴ It is this feature which enables us to consider for the first time the spectrum of a large realistic anharmonic molecular system. The two major difficulties with our method are (i) calculation (A) is perturbative in U . The similarity of spectra (B) and (C) strongly support the validity of this approximation for the present system. (ii) The nonuniqueness of the potential surface on which the classical trajectories need to be calculated. This is a fundamental problem,

which arises from the fact that the spectrum is a non-analytic function of \hbar .¹ We have carefully examined the effects of both problems by calculating the vibronic structure of the same molecule using an approximate model for the excited surface which includes frequency shifts, origin shifts, and Dushinsky rotations. The resulting spectra are very similar (but not identical) to the exact quantum mechanical spectrum for this model.⁸ This provides another evidence for the applicability of the present method.

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Phonon echo in organic solids^{a)}

J. Swiatkiewicz,^{b)} G. B. Talapatra, R. J. Kurland, and P. N. Prasad

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

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We report here the first observation of phonon echo in organic solids. The phonon echo (also called polarization echo) has previously been investigated for metals and inorganic ferroelectric and piezoelectric materials.¹⁻³ In view of the growing interest in the use of organic piezoelectric materials as nonlinear devices,⁴ the study of phonon echos in organic piezoelectric systems is significant. We report the observation of phonon echos in powders of an organic piezoelectric: *d*-tartaric acid.

The procedure used to produce a phonon echo in a piezoelectric material is to apply two rf pulses, separated by a time delay τ . Via the piezoelastic properties of the material, the rf pulses generate acoustic oscillations. A coherent emission (echo) after the second pulse is produced at time 2τ , if appropriate conditions of particle size and number are met. The phonon echo can provide valuable information regarding the propagation and relaxation of acoustic waves in the frequency range 5 MHz–10 GHz. The method can also be used on single crystal samples.

For our experiment a Bruker B-KR 321 s variable frequency (16–62 MHz) pulsed NMR spectrometer was

used. The rf pulses were capacitively coupled to the sample by a 1.5 in. diam parallel plate condenser, with

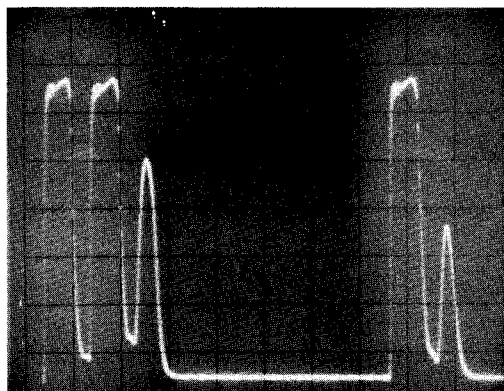


FIG. 1. Oscilloscope photograph of the observed phonon echo in a precipitated *d*-tartaric acid powder (particle diameter $< 30 \mu\text{m}$) at room temperature and atmospheric pressure. The rf frequency used is 20 MHz, the pulse width is $2 \mu\text{s}$ and the separation (τ) between the two pulses for the two pulse echo is $20 \mu\text{s}$. The third pulse for the stimulated pulse echo is applied at $t = 75 \mu\text{s}$.