Gas-Phase Molecular Dynamics: Vibrational Dynamics of Polyatomic Molecules

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Project Scope

The goal of this research is the understanding of elementary chemical and physical processes important in the combustion of fossil fuels. Interest centers on reactions and properties of short-lived chemical intermediates. High-resolution, high-sensitivity, laser absorption methods are augmented by high-temperature, flow-tube reaction kinetics studies with mass-spectrometric sampling. These experiments provide information on the energy levels, structures and reactivity of molecular free radical species and, in turn, provide new tools for the study of energy flow and chemical bond cleavage in radicals involved in chemical systems. The experimental work is supported by theoretical studies using time-dependent quantum wavepacket calculations, which provide insight into energy flow among the vibrational modes of polyatomic molecules and interference effects in multiple-surface dynamics.

Recent Progress

Vibrational dynamics of "planar acetylene"

The acetylene molecule (HCCH) is one of the simplest hydrocarbon molecules, yet it has quite rich and complex molecular spectroscopy. [1] We have extended our previous studies of "linear acetylene", [2] a (3D) stretching-only model, to "planar acetylene" by inclusion of the two (nondegenerate) bending modes into a five-mode model. This model exhibits quartic anharmonic resonances that complicate the vibrational dynamics, and has a much higher density of vibrational states than the 3D model. The 5D wavefunction of J=0 planar HCCH was represented using a direct-product plane-wave discrete variable representation (DVR) of nearly 300,000 points. The molecular symmetry of planar acetylene is described by the C_{2v} point group, and the dipole moment function transforms as B_2. We have computed the vibrational eigenvalues and eigenfunctions of A_1 and B_2 symmetry for this model up to *ca.* 17,000 cm^{-1} above the potential minimum. The vibrational eigenfunctions of the model are extremely useful in studies of the vibrational spectroscopy and dynamics in three distinct ways: (1) they are essential for simulating the vibrational spectra; (2) they allow us to project a time-dependent wavepacket to obtain the evolution of the vibrational state populations; and (3) they can serve as an "essential states" basis in simulations of the vibrational dynamics that is much more compact than the full DVR grid from which they are derived.

Wavepacket propagation. In simulations of the vibrational dynamics, it is necessary to solve the time-dependent Schrödinger equation. Either a time-dependent or time-independent potential function can be handled by the Lanczos propagator, which involves the short-time expansion of the wavepacket in a (small) Krylov space $\{|\ell_k\rangle\}$ generated from the wavepacket itself *via* a three-term recursion relation. At each point n on the DVR grid with continuous coordinate eigenfunctions $\{|u_n\rangle\}$, the wavepacket at time $t + \Delta t$ is given by

$$\langle u_n | \Psi(t + \Delta t)\rangle = \sum_{m=1}^{N_t}\langle u_n | \ell_m\rangle \sum_{k=1}^{N_t}\langle \ell_m | e_k\rangle \exp\left(-\frac{i}{\hbar}E_k\Delta t\right)\langle e_k | \ell_1\rangle\langle \ell_1 | \Psi(t)\rangle$$

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where $|\ell_1\rangle$ is the normalized $|\Psi(t)\rangle$, and $\{|e_k\rangle\}$ is the set of eigenvectors, with corresponding eigenvalues $\{E_k\}$, of the time average of $\hat{H}(t)$ in the interval $(t, t+\Delta t)$ represented in the Krylov space $\{|\ell_m\rangle\}$. The error in the Lanczos propagator is proportional to $(\Delta t)^{N_L}$, so it can be made negligible compared to round-off error for relatively small values of N_L (e.g., $N_L = 12$).

Obtaining a large set of vibrational eigenfunctions as a secondary "essential-states" basis. The Lanczos propagator can be used to compute the time-correlation function of an arbitrary initial wavepacket, $\langle\Psi(0)|\Psi(t)\rangle$. The eigenvalue spectrum of the eigenstates contained in the initial wavepacket is then obtained from the Fourier transform of the time-correlation function. Separate symmetry-adapted autocorrelation functions can be obtained for eigenstates of all symmetry species in a single wavepacket propagation. Accurate energy eigenvalues and their corresponding eigenfunctions can be obtained one at a time by propagating the initial wavepacket in negative imaginary time using the *ad hoc* energy-filtered propagator

$$\hat{U}(0, -i\Delta t) = \exp\left(-\left|\hat{H} - E_{filter}\right|\frac{\Delta t}{\hbar}\right)$$

and repetitively renormalizing. Here E_{filter} is the estimated eigenvalue, and repeated application of this propagator causes the initial wavepacket to decay to the eigenfunction corresponding to the eigenvalue closest to E_{filter}. The absolute value operator, meaningful only in the context of the Lanczos propagator, discriminates well between closely spaced eigenvalues.

For highly excited and closely spaced eigenstates, the energy-filtered, imaginary-time propagation method becomes too laborious. An alternative is filter-diagonalization using the Chebyshev propagator. We have, in collaboration with R. Chen and H. Guo, successfully applied filter-diagonalization to obtain a large number of accurate vibrational eigenvalues of planar acetylene, but the construction of more than a few of the corresponding eigenfunctions, though straightforward, was not practical. It became necessary to find a more efficient way to obtain a fairly large number of relatively accurate eigenfunctions.

We partitioned the vibrational modes of the 5D model into two categories: stretches and bends. These two categories of vibrational states are coupled only weakly by quartic anharmonic resonances in acetylene. The eigenstates of the three stretching modes were computed on the 3D DVR sub-grid defined by restricting the bending angles to their equilibrium values. Also those of the two bending modes were computed on an analogous

Figure 1. Energy eigenvalues of "planar acetylene" having A_1 and B_2 symmetry obtained by a sequential diagonalization/truncation approach.

2D DVR sub-grid. Each group of states was sorted by symmetry and truncated. Diagonalization of symmetry-adapted direct products of stretching and bending states yielded a set of 200 eigenstates of A_1 symmetry and 162 eigenstates of B_2 symmetry. The energy eigenvalues of these states are shown in Fig. 1. The corresponding eigenfunctions were subsequently used as an "essential states" basis in successful simulations of the laser manipulation (control) of the vibrational dynamics of planar acetylene. The laser pulse characteristics were optimized using the essential-states basis, then verified using the full DVR grid. For example, the selective excitation of the excited $(0,3,0,0,0)$ A_1 CC-stretch state from the ground
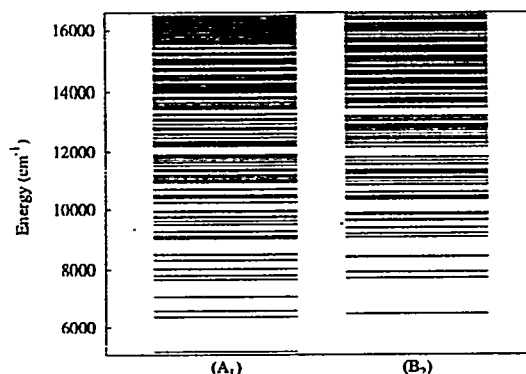
(0,0,0,0,0) A_1 state *via* the (0,0,1,0,0) B_2 fundamental CH antisymmetric stretch state was simulated to have an 85% yield despite being complicated by field-induced avoided crossings.

Wavepacket Dynamics of ICN Photodissociation Revisited

In conjunction with experimental Doppler lineshape studies by Hall, North and Costen in our group, we have attempted to extend the previous wavepacket treatments [3, 4] of ICN photodissociation on the *ab initio* potential energy surfaces of Amatatsu *et al.* [5] Non-adiabatic transitions at the avoided crossing between the $^3\Pi_{0^+}$ (A') state, which correlates diabatically to the I* channel, and the A' component of the $^1\Pi_1$ state, which correlates diabatically to the I channel, complicate the assignment of anisotropies of selected product states. We assume that a distinct polarization (parallel or perpendicular) is associated with each element of population, and that the type of polarization is unaffected by the wavepacket dynamics. In general, this means that the nuclear wavefunction in each electronic state is analogous to a "spinor", *i.e.*, a two-component wavefunction with one component corresponding to "parallel polarization" and the other to "perpendicular polarization." We need not, however, consider ten nuclear wavefunctions: since only two electronic states can exchange population, only those need to be described by two components.

We write the time-dependent wavefunction for the system as

$$\left|\Psi(t)\right\rangle = \sum_{p=1}^{2}\left|p\right\rangle\sum_{k=1}^{5}\left|k\right\rangle\left|\Phi_{kp}(t)\right\rangle$$

where, as discussed above, the sum over polarization functions $\left|p\right\rangle$ can be suppressed for all but two electronic states. Note that $\left|\Phi_{kp}(t)\right\rangle$ is one component of a two-component, time-dependent nuclear wavefunction in the kth electronic state. We assume the Hamiltonian operator for the system is $\hat{H} = \hat{H}_{el} + \hat{T}_{nuc}$ and that we can express the diabatic representation of the electronic states as $\left\langle n\right|\hat{H}_{el}\left|k\right\rangle = V_{nk}$ with all off-diagonal V_{nk} equal to zero except that connecting the $^3\Pi_{0^+}$ (A') and $^1\Pi_1$ (A') electronic states. Substituting into the time-dependent Schrödinger equation and left-multiplying by $\left\langle n\right|\left\langle p'\right|$ and using the orthonormality property $\left\langle p\middle|p'\right\rangle = \delta_{pp'}$, we have

$$\frac{\partial}{\partial t}\left|\Phi_{np'}(t)\right\rangle = \frac{-i}{\hbar}\sum_{k=1}^{5}\left(\hat{T}_{nuc}\delta_{nk} + V_{nk}\right)\left|\Phi_{kp'}(t)\right\rangle$$

which shows that the non-adiabatic coupling can transfer population only between states with the same polarization. This is the essential new feature of the present treatment, and it allows us to compute the polarization anisotropies of the I* and I channels in ICN photodissociation as well as the rotational-state-dependent anisotropies in a given product channel.

Attempts to compare the results of these new calculations with experiment reveal deficiencies in the *ab initio* potential energy surfaces. Experimental Doppler lineshape studies indicate that the dissociation energy of the calculated ground state is approximately 0.5 eV too small. Employing the same (incorrect) ground-state dissocation energy used in the previous calculations of Qian *et al.* introduces an artifact: the state distributions for a given photodissociation wavelength have an incorrect (spuriously high) energetic cutoff. The comparison between theoretical and experimental rotational-state-dependent anisotropy parameters also reveal serious deficiencies in the potential energy surfaces.

In making the improvements discussed above in the wavepacket calculations of ICN photodissociation, we have caused the agreement between theory and the most definitive experiments to become worse. Both sides of the theoretical absorption band behave in a qualitatively incorrect manner owing to deficiencies in the potential energy surfaces. While the theoretical description of the non-adiabatic

coupling between the $^3\Pi_u$ and $^1\Pi_u$ states seems qualitatively correct, the theory appears to overestimate the relative contribution of the $^1\Pi_u$ state. Nevertheless, our approach allows us to begin to explore multiple-surface interference effects in experimental dynamics.

Future Plans

One of the primary experimental thrusts of our research group is the characterization of the structure and vibrational spectroscopy of molecular free radicals (e.g., CH_2 and CH_3CH_2). A new theoretical thrust will be to contribute to the understanding of the vibrational spectra of some of the radical species of interest by calculating the spectral features from potential energy surfaces using quantum mechanical methods. The relevant potential functions for selected motions (e.g., the CH_3 rotation, the CH_2 wag and the CC stretch in CH_3CH_2) will be computed using one or more of the electronic structure codes in widespread use. We will then build model Hamiltonians for describing the restricted vibrational motion, and calculate vibrational eigenvalues using direct-product discrete variable representations (DVRs) as a basis. We will also pursue additional acetylene studies using an improved potential energy surface [6] and will continue our investigations of interference effects in multiple-surface dynamics.

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Acknowledgement

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