EVOLUTION OF SIZE EFFECTS IN CHEMICAL DYNAMICS

Part 1

ADVANCES IN CHEMICAL PHYSICS
VOLUME LXX

Edited by

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

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STUART A. RICE
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LEVEL STRUCTURE AND DYNAMICS FROM DIATOMICS TO CLUSTERS*

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I. INTRODUCTION

In our 1981 review,¹ we suggested that analyses using a microscopic description of dynamics would increasingly influence our interpretation of the properties of large systems; that the merging of the microscopic and macroscopic methods of analysis would lead to an understanding of the gradual transition from the behavior characteristic of the intramolecular dynamics of

* Work supported by the U.S.–Israel Binational Science Foundation, The U.S. Army European Research Office, The U.S. Air Force Office of Scientific Research (AFOSR), and the U.S. National Science Foundation.
an isolated small molecule to that characteristic of the statistical dynamics of a condensed phase. In particular, processes on surfaces\(^2\) and interfaces and in molecular clusters were expected to provide the bridge whereby one could examine electronic structure, vibrational and electronic excitations, and intramolecular dynamics in large but finite systems\(^3\) as a function of the size of the system.

This volume provides an account of some of the results of studies that illustrate the expectations previously expressed. Indeed, our understanding of the transition from small- to large-system dynamics has been enriched to such an extent that the basic results are already to be found in primers of chemical reactivity.\(^4\) In the same period we have also witnessed a qualitative improvement in our knowledge of the dynamics of small molecules. As is always the case, much of the progress that has been made is derived from new experimental techniques used in an imaginative fashion. The most important new experimental techniques use various combinations of lasers and supersonic beams to explore chemically interesting questions. For smaller systems, our understanding of chemical reactivity and, in particular, our ability to control and probe collision processes, has been advanced significantly. We consider first the impact of new spectroscopic techniques\(^5\) on our knowledge of intramolecular dynamics, including the new theoretical techniques that are being developed to examine the large amounts of data produced by high-resolution spectroscopy at chemically significant levels of excitation. We then examine the level structure and properties of clusters. The dynamics of nuclear motion, the nature of electronic excitations, and the electronic–vibrational relaxation phenomena in nonmetallic clusters, provide a wealth of novel information\(^3\) that helps bridge the different interpretations of the dynamics of isolated molecules and condensed phases.

II. HIGH-RESOLUTION SPECTROSCOPY AND INTRAMOLECULAR DYNAMICS

Direct high-overtone excitation\(^6,7,9\) of a molecule reaches states with local-mode character that carry significant transition strength from the ground state. Much of the extent theoretical effort has been directed at computing the corresponding level structure,\(^16\) the nature of the optically prepared state,\(^10,24,25\) and the ensuing intramolecular dynamics.\(^26\) Brute force quantum-mechanical computations of the spectrum run into the difficulty that the size of the Hamiltonian matrix required to achieve convergence for these high-lying states taxes the abilities of present day computers. Semiclassical methods of analysis clearly have an advantage in this case. It remains to be seen, however, how well the procedure of adiabatic switching\(^35\) can "zero in" on the eigenstate of interest for Hamiltonians of realistic com-
plexity. Many of the theoretical studies have been carried out on model systems for which key terms such as Coriolis coupling are neglected, even though said coupling has been clearly implicated in intra-molecular energy redistribution. This is also the case for the algebraic approach, which even in zeroth order treats the oscillations as anharmonic and accounts for Fermi and for Darling–Dennison (or, equivalently, for local-mode) coupling between the anharmonic oscillators. However, the algebraic method has not yet been generalized to include vibration–rotational coupling, nor has it been applied to realistic spectra.

Spectroscopic studies at even higher levels of excitation on the ground-state potential energy surface is possible by an indirect route. In stimulated emission pumping (SEP) an initial state is laser pumped to a specific, single, rotation–vibration level of an electronically excited state. A second laser stimulates the emission from the electronically excited state down to an excited level of the ground electronic state. The SEP spectrum of $C_2H_2$, for example, is quite different from that obtained using direct overtone excitation. The low-resolution ($\sim 0.3 \text{ cm}^{-1}$) SEP spectrum at about 26,500 cm$^{-1}$ shows a series of features with a density of about 0.6 per cm$^{-1}$. Higher-resolution spectroscopy reveals that each feature is a clump of lines with a density of about 8 per cm$^{-1}$ (Fig. 1). The usual spectroscopic methods of assignment of lines are unlikely to be useful in practice (and possibly even in principle). Statistical tests based on near-neighbor spacing distributions can be applied but are complicated by level congestion. A new approach is to examine the "survival probability" $P(t)$, that is, the square modulus of the Fourier transform of the spectrum $I(\omega)$,

$$P(t) = \left| \int I(\omega) \exp(-i\omega t) \, dt \right|^2$$

For a "stick spectrum" of $\mu$ lines where $y_n$ is the intensity of the $n$th transition at the frequency $\omega_n$, $I(\omega) = \sum_{n=1}^{N} y_n \delta(\omega - \omega_n)$, there are two contributions to $P(t)$:

$$P(t) = \sum_n y_n^2 + \sum_{n \neq m} y_n y_m^* \exp[i(\omega_n - \omega_m)t]$$

Upon taking an ensemble average, the first term, which contributes only at the origin, yields $N^2 \langle y^2 \rangle$, where $\langle y^2 \rangle$ is the averaged intensity. The average value of the second term depends in an essential way on the correlation between positions of the different lines. On the assumptions that (1) the distributions of intensity and of positions are independent and (2) that the probability to find another line at a distance $\Delta \omega$ from the first line depends
Figure 1. SEP spectrum of C\textsubscript{2}H\textsubscript{2} at about 26,500 cm\textsuperscript{-1} of vibrational excitation in the ground electronic state. [Adapted from J. P. Pique, Y. Chen, R. W. Field and J. L. Kinsey, Phys. Rev. Lett. \textbf{58}, 475 (1987).] (a) Low-resolution (~0.3 cm\textsuperscript{-1}) spectrum; (b) high-resolution (~0.05 cm\textsuperscript{-1}) spectrum. Each feature in (a) is resolved into a series of lines. The overall "envelope" variation in intensity in (b) is the "clump" structure seen in (a).

only on the frequency difference \( \Delta \omega \) (and not on the absolute positions), the second term of Eq. (2) yields \( N \langle y^2 \rangle [1 - G b_2(t)] \), where \( b_2(t) \) is the Fourier transform of the cluster function\textsuperscript{54} \( Y_2(\omega) \). From the computation of \( P(t) \) one can therefore extract the value of \( G \equiv \langle y \rangle^2 / \langle y^2 \rangle \) (provided the number, \( N \), of lines has been counted) and the \( t \) dependence of \( b_2(t) \). We expect \( b_2(t) \) to decline from unity with a width, \( t_\epsilon \), which is inverse to the frequency range of level correlations. For an anharmonic but "regular" spectrum, the level positions are uncorrelated. In the limit when the corresponding classical motion is chaotic, the correlation range is the mean spacing, so that \( t_\epsilon = \rho/c \).

\* The cluster function is defined\textsuperscript{54} such that for an infinite spectrum with unit mean spacing \( \frac{1}{2} (1 - Y_2(\omega_n, \omega_m)) d\omega_n d\omega_m \) is the probability of finding two transitions in the intervals \( \omega_n, \omega_n + d\omega_n \) and \( \omega_m, \omega_m + d\omega_m \).
where $\rho$ is the density of states. In general, $t_c = \rho_c/c$, where $\rho_c$ is the density of correlated states. Figure 2 shows the results for $P(t)$ for the high-resolution spectrum of C$_2$H$_2$. The overall decline of $P(t)$ with time is due to the envelope shape of the clump of states. The correlation hole following the fast decay [the first term in (2)] is evident but is not very deep, since $G < 1$, $t_c \approx 45$ ps, and $\rho_c \approx \rho/6$. At a somewhat higher energy even more lines are strongly correlated.

In Fig. 2 we have considered the properties of the distribution of line positions irrespective of their intensities. Should we not also examine the distribution of intensity, irrespective of position? This can be done by dividing the ordinate in Fig. 1 into bins and counting the number of transitions whose intensity falls within any given bin. The results$^{55}$ are shown in Fig. 3 together with a fit to the functional form$^{56}$

$$P(y) = y^{(v/2)-1} \exp\left(\frac{-vy}{2}\frac{2\langle y \rangle}{v}\right)^{v/2} \Gamma\left(\frac{v}{2}\right)$$

(3)

for which $G = \langle y \rangle^2/\langle y^2 \rangle = v/(v + 2)$. The value of $v$ is sensitive to the precise choice of the base line of zero intensity. However, sensibly independent of this choice, $v \geq 3$ and so $G \geq 0.6$. For a quantal spectrum where the corresponding classical motion is chaotic, one expects$^{56,57}$ $v = 1$ or $G = \frac{1}{2}$. This is not the case for C$_2$H$_2$ at 26,500 cm$^{-1}$, as is also evident from the analysis of Fig. 2. This is, however, the case for the spectrum$^{12}$ of NO$_2$ at 17,000 cm$^{-1}$, as shown in Fig. 4.

Another route for accessing the ground potential energy surface at energies at or even above dissociation$^{58,59}$ is via a nonradiative transition from an excited electronic state. One would then expect fluctuations in the lifetimes of the predissociating states much as the transition strengths fluctuate for the
Figure 3. Statistical analysis of the intensity distribution of the high-resolution spectrum of C$_2$H$_2$ at about 26,500 cm$^{-1}$, including nearly 4000 lines. (Adapted from Ref. 55.) The solid line is the maximum entropy distribution (cf. Ref. 56) given by Eq. (3) with $v = 3.2$.

Figure 4. Same as Fig. 3 but for NO$_2$ (data of Ref. 12). Here the fit by Eq. (3) shows that no constraints are needed ($v \approx 1$) so that the fluctuations are as random as possible. (Adapted from Ref. 55.)
bound-state spectra. For D₂CO, an order of magnitude variation in rates is observed²⁸ for states within a 0.2 cm⁻¹ energy range at about 28,000 cm⁻¹. For SiH₃, fluorescence lifetimes of individual ro-vibronic states at 17,000 cm⁻¹ vary²⁹ by almost three orders of magnitude and can be well fitted⁶⁰ by a distribution of the type (3) with n = 1. An essentially statistical intensity distribution is also found⁶⁰ for benzene in the "channel three" region.⁶¹

III. LASER STUDIES OF CHEMICAL REACTIVITY

That lasers have played a key role as promoters and as probes of chemical reactions is well known and extensively documented.¹⁴,⁶²–⁷² In many of these applications the laser is employed as an intense, nearly monochromatic, light source whose characteristics ensure species selectivity, a well-characterized spectroscopy, and adequate intensity for multiphoton processes. Some possible applications, notably "laser-assisted collisions"⁷³,⁷⁴ and transition-state spectroscopy,⁷⁵,⁷⁶ are yet in their infancy, but the extant studies already suggest considerable promise for influencing and probing chemical reactions.

In recent experiments additional properties of lasers have been used in an essential way and these have opened up new avenues for exploring and understanding chemical reactivity. The first of these properties is the seemingly obvious spatial collimation characteristic of laser light. Doppler shift measurements⁷⁷–⁸⁰ have now successfully been used to deconvolute spectral line shapes and also to measure the speed distribution of reaction products along the light beam direction (Fig. 5). Another property of laser radiation that is beginning to contribute to our understanding of steric aspects of chemical

\[
\text{PH}_3\left(\tilde{X}^1\text{A}_1\right) + h\nu(193.3 \text{ nm}) \rightarrow \text{PH}_2 + \text{H} \\
E = h\nu - Q_f(\text{PH}_2 - \text{H}) = E_T + E_i
\]

Figure 5. H atom kinetic energy distribution from the photolysis of PH₃ at 193.3 nm as deduced from Doppler profiles (using Lyman-α radiation). The two curves bound the range of acceptable fit to the measured profiles. [Adapted from Z. Xu, B. Koplitz, S. Buelow, D. Baugh, and C. Wittig, Chem. Phys. Lett. 127, 534 (1986).]
Figure 6. Photodissociation of the CO$_2$HBr van der Waals molecule. (a) The proposed structure of the adduct. At the minimum all atoms are collinear but the restoring force for the bending (as shown) is small. (b) At the instant of dissociation. The H atom is directed into a narrow cone about the OCO axis. (c) The measured OH ($v = 0$) rotational distribution under bulk conditions and from the photolysis of the adduct. The solid curve is computed assuming a linear rotational surprisal and the $\theta_R$ values shown. The OH distribution from the dissociation of the adduct is rotationally cold. [Adapted from S. Buelow, M. Noble, H. Radhakrishnan, H. Reisler, C. Wittig and G. Hancock, J. Phys. Chem. 90, 1015 (1986).]
reactions is polarization. The polarization of a light beam can be used to prepare aligned reagents and also to probe the alignment of the products. Stereoselectivity can also be studied by photodissociation of a van der Waals adduct prepared in a supersonic beam. Figure 6 shows the proposed structure of CO₂HBr with the hydrogen atom adjacent to the oxygen. Upon photolysis of HBr, the velocity vector of the H atom is confined to a cone about the OCO axis. The OH vibrational distribution from the reaction

\[ \text{OCO} + \text{H} \rightarrow \text{CO} + \text{OH} \]

is different (i.e., colder) than that observed when the velocity vector of the hot H atom is randomly oriented (Fig. 6). In the past, lasers have been used to select the initial states of the reagents and to probe the states of the products formed, which are the "scalar" characteristics of the reaction dynamics. With the newer experiments, vector characteristics are being selected and/or probed.

Another aspect of chemical reactivity that is receiving considerable attention is the reaction of electronically excited species. Questions of orbital stereoselectivity are likely to keep both experimentalists and theorists busy for some time to come.

Laser pulses of short duration have been used to prepare, in bulk samples, a large initial concentration of reactive atoms or radicals. More recently, by using a second probe laser pulse, delayed with respect to the initiation pulse, it is found possible to monitor reaction products formed after a single collision of the reactive species. The recent progress in experimental studies of the H + H₂ exchange reaction is due to this technique. It is finally possible (Fig. 7) to report agreement between experiments and for this fundamental chemical reaction.

Unimolecular dissociation can also be studied in this fashion. The first pulse provides the energy and the second probes the dissociation products in real time. To achieve the time resolution sufficient to monitor the unimolecular dissociation, both pulses need to be ultrashort. The absolute unimolecular rate constant into any given internal state of the product can be so measured. Relative rates of reaction from an initial state into a set of final states have been available for some time since they are provided by the measurement of the products' state distribution. With the new techniques, the magnitude of the rate can be measured. Such results for neutrals (and also measurements of lifetimes of metastable multiphoton produced ions) will test in detail our theoretical understanding of unimolecular reactions. The fundamental concept that a bottleneck separates the energy rich molecule from the products needs to be reexamined. Nor is it going to be enough to stand, a la RRKM, at the bottleneck and count phase points as they cross.
Rather, it will be necessary to include the exit valley interactions, so as to account for the partitioning into specific final states.

Theorists have also considered the yet to be tapped capabilities of lasers and have recently centered attention on coherence effects. Consider the probability to observe a set of final states $\rho_f$ following optical excitation of an initial state $|i\rangle$ by a weak field. This can be written as

$$P_{fi} = \lim_{T \to \infty} \frac{1}{T} \int_0^T \text{Tr}[\rho_f \rho_i(t)] \, dt$$

(4)

where

$$\rho_i(t) = U(t) \mu |i\rangle \langle i| \mu^\dagger U^\dagger(t)$$

(5)

with $U(t)$ the evolution operator of the unperturbed molecule and $\mu$ is the dipole operator. Introducing a set of energy eigenstates for the molecule,

$$U(t)|n\rangle = \exp(-iE_n t/\hbar) |n\rangle$$

(6)
Figure 8. A picosecond laser experiment to determine the photodissociation lifetime of CH$_3$I$^*$. [Adapted from J. L. Knee, L. R. Khundar, and A. H. Zewail, J. Chem. Phys. 83, 1996 (1985).]
(a) An outline of the experiment: a picosecond laser pulse pumps CH$_3$I to the repulsive $\tilde{A}$ state. The I (or I*) atoms are detected as ions using a picosecond laser pulse for resonance-enhanced multiphoton ionization. (b) The I$^+$ ion signal. Deconvolution yields a lifetime of $\leq 0.5$ ps.
one can write (4) as

\[ P_{fi} = \lim_{T \to \infty} \frac{1}{T} \int_0^T \sum_n \sum_m \langle n | \rho_f | m \rangle \exp[i(E_n - E_m)t/\hbar] \langle m | \rho_i | n \rangle \]  

and, after integration (which cancels all off-diagonal terms in the \( T \to \infty \) limit), we obtain

\[ P_{fi} = \sum_n \langle n | \rho_f | n \rangle \langle n | \rho_i | n \rangle \]  

where \( \rho_i = \rho_i(0) \). The result (8) is purely diagonal and carries on phase information. To achieve photoselectivity, that is, to be able to influence the magnitude of \( P_{fi} \), it is necessary to remove one or more of the restrictions imposed in the derivation of (8). The conditions used in the derivation of (8) are: (1) The external field is weak, so that the excitation can be described by first-order perturbation theory. This need not be the case. (2) The molecule evolves unperturbed following excitation. This can be modified by using a coherent sequence of pulses. For example, suppose the first ultra-short pulse promotes the molecule to an excited electronic state surface; so far, as in (4). However, rather than being allowed to dissociate from the upper state, a second laser pulse brings the molecule back down to the ground potential energy surface. By controlling the ultrashort delay between the two pulses, one determines the extent of propagation on the upper surface. Different propagation times can lead to a selective dissociation pathway on the lower potential energy surface.

Another theoretical possibility is to use a coherent superposition of initial states. Very schematically, one would write

\[ |i\rangle = C_1 |1\rangle + C_2 |2\rangle \]  

so that four terms contribute to \( \langle n | \rho_i | n \rangle \):

\[ \langle n | \rho_i | n \rangle = \langle n | \mu | 1 \rangle^2 C_1^2 + \langle n | \mu | 2 \rangle^2 C_2^2 + \langle n | \mu | 1 \rangle \langle 2 | \mu | n \rangle C_1 C_2^* + \langle n | \mu | 2 \rangle \langle 1 | \mu | n \rangle C_2^* C_1. \]

By controlling the phase relations in the initial state (i.e., the phase difference between \( C_1 \) and \( C_2 \)) and the relative intensity of the two lasers used to photolyze the eigenstates \( |1\rangle \) and \( |2\rangle \), one can influence the branching factors into different product states (Fig. 10).
Figure 9. Selectivity of photodissociation controlled using a coherent pulse sequence. [Adapted from D. J. Tannor, R. Kosloff, and S. A. Rice, J. Chem. Phys. 85, 5805 (1986).] The system is pumped at $t = 0$ to an excited electronic state surface on which it propagates for a time $T$ and is then brought down to the ground surface. Two classical trajectories are shown for (a) $T = 600$ au, (b) $T = 2100$ au. The computations are for vertical up and down transitions. Parts (c) and (d) show the corresponding quantum-mechanical results. The different plots are for (c): 0, 800, 1000 au propagation on the ground-state surface and (d): 0, 1000, 1200 au propagation on the ground-state surface.
Figure 10. Photodissociation of an initial coherent linear superposition of states in CH$_3$I. [Adapted from P. Brumer and M. Shapiro, Chem. Phys. Lett. 123, (1986).] (a) A cut of the potential energy surface along the dissociation coordinate. The figure shows the two bound states [cf. (9)] that are photodissociated (to the same total energy). (b) Contour plot of the yield of ground state I atoms as a function of the relative intensity ($S$) of the two photodissociating lasers and of the phase difference.