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Energy and Chemical Change

Final Progress Report

submitted to

The Air Force Office of Scientific Research

by

James L. Kinsey and Raphael D. Levine
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January 1, 1993

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Houston, Tx 77030

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall object of this project was a better theoretical understanding of the dynamics of energy rich molecules in both bound and unbound states. Particular attention was to be given to the understanding and elucidation of selectivity in the role of initial energy acquisition and its subsequent disposal. Some effort was directed at the understanding of such selectivity not only for isolated molecules but also for molecule-surface collisions. Two novel methodologies were developed and brought to fruition during these studies. One is the use of algebraic Hamiltonians for the description of high overtones (and hence highly anharmonic) energy rich states and the determination of the potential energy from observed spectra in this way. Very extensive work has demonstrated the realistic feasibility of this approach for triatomic molecules (both linear and bent) and for linear tetratomic molecules. A complete summary of this approach has just been written up for publication as a book which includes tables of parameters of algebraic Hamiltonians for a

variety of molecules. The other new theoretical methodology studied in this program is the use of the maximum entropy information theory approach for the description of the intramolecular dynamics of energy rich molecules both below and above the dissociation limit. In particular, this approach was used to 'invert' an observed Raman excitation spectrum, that is, to extract from the frequency spectrum the time evolution of the system. Other techniques, as needed, were also used in the studies of the time evolution. In particular, the use of the algebraic approach towards the elucidation of the separation of time scales and its relation to the restricted sampling of the available phase space prior to dissociation. Extensive runs of classical trajectories were also performed so as to demonstrate the incomplete sampling of phase space even at energies well above dissociation. The selectivity studied for surface processes focused on the interplay between energetic and steric factors. It was shown that, as in the gas phase, one can usefully distinguish between processes whose efficiency either decreases or increases with the surface. The steric factors which were discussed include the shape of the incident molecule and the 'structure sensitivity' of the process to the particular face of the surface.

1. INTRODUCTION

The overall object of this project was a better theoretical understanding of the dynamics of energy rich molecules in both bound and unbound states. Particular attention was to be given to the understanding and elucidation of selectivity in the role of initial energy acquisition and its subsequent disposal. Some effort was directed at the understanding of such selectivity not only for isolated molecules but also for molecule-surface collisions. Two novel methodologies were developed and brought to fruition during these studies. One is the use of algebraic Hamiltonians for the description of high overtones (and hence highly anharmonic) energy rich states and the determination of the potential energy from observed spectra in this way. Very extensive work has demonstrated the realistic feasibility of this approach for triatomic molecules (both linear and bent) and for linear tetratomic molecules. A complete summary of this approach has just been written up for publiation as a book which includes tables of parameters of algebraic Hamiltonians for a variety of molecules. The first and last chapters of this book are included in Appendix A. The other new theoretical methodology studied in this program is the use of the maximum entropy information theory approach for the description of the intramolecular dynamics of energy rich molecules both below and above the dissociation limit. In particular, this approach was used to 'invert' an observed Raman excitation spectrum, that is, to extract from the frequency spectrum the time evolution of the system. A fully detailed report on this work is already available. It is however quite lengthy so the preliminary announcement of these results is included as an Appendix B. Other techniques, as needed, were also used in the studies of the time evolution. In particular, the use of the algebraic approach towards the elucidation of the separation of time scales and its relation to the restricted sampling of the available phase space prior to dissociation. Extensive runs of classical trajectories were also performed so as to demonstrate the incomplete sampling of phase space even at energies well above dissociation. The selectivity studied for surface processes focused on the interplay between energetic and steric factors. To begin with, it was shown that, as in the gas phase, one can usefully distinguish between processes whose efficiency either decreases or increases with the surface. The steric factors which were discussed include the shape of the incident molecule and the 'structure sensitivity' of the process to the particular face of the surface.

We turn now to a discussion of specific results. The reference numbers are to the list of publications, Section 6 of this report.

2. Algebraic Hamiltonian

At the conclusion of this proposal it is possible to state that the algebraic approach has been fully validated for triatomics. This includes not only all known vibration-vibration coupling but also vibration-rotation coupling. The transcription from an algebraic to a geometrical picture is fully at hand [4, Ch. 7 of 31] and the connection with intramolecular dynamics is being explored [26]. Our plans for the future in that direction are outlined in Appendix A.

3. Intramolecular Dynamics

Three reviews [1,18,25] provide a summary of our work up to a year ago. These are quite detailed and cover the entire gamut of our activities so it would be superfluous to repear it and we include the latest of those as Appendix C. Instead, we draw attention to the most recent work (for a short report, see Appendix B) where the maximum entropy formalism has been effectively employed to represent spectra. Not discussed therein are implications towards a separation of time scales. This is shown in figure 8.1 of Appendix A. The connection to our previous AFOSR supported work on intensity fluctuations has been firmly established and is in preparation for publication. The different aspects of intramolecular dynamics as discussed in the original proposal are all extensively represented in the list of publications.

4. Sticking and Dissociation in Molecule-Surface Collision

Following the experimental demonstration, by the late R.B. Bernstein, of a large steric effect in the sticking of molecules to surfaces and taking cognizance of the AFOSR interest in selectivity of surface processes, we attempted a theoretical discussion of this effect [6]. The theory clearly predicted a decrease of the effect with increasing collision energy with the surface. We therefore checked the theory for dissociation processes whose probability is known to rise steeply past the energetic threshold [13]. When this could be explained we examined the sensitivity to the structure of the surface [15,23]. Work is continuing in this direction, supported by a PRF grant to Dr. Farrelly, who is by now in Utah.

5. Cooperation with Other AFOSR Projects

Two papers are a result of discussions with other AFOSR supported scientists, discussions which took place at the annual contractors meetings. Paper [7] is a discussion of a possible experimental test of the extent of geometrical randomization prior to dissociation. Papers [21] and [30] discuss the extent of energy randomization following selective excitation. The groups of Professors Thompson and Raff have since done more work in that direction.

6. Published or Accepted Papers

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2. Y.M. Engel and R.D. Levine
   Vibration-Vibration Resonance Conditions in Intramolecular Classical Dynamics of Triatomic and Larger Molecules, *Chem. Phys. Lett.* 164, 270 (1989).
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   Nearest Neighbor Level Spacing Distributions: On the Transition from the Regular to the Chaotic Regime, *Phys. Rev.* A40, 5277 (1989).
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   Construction of Triatomic Potentials from Algebraic Hamiltonians which Represent Stretching Vibrational Overtones, *J. Mol. Struct. (Theochem.)* 199, 201 (1989).
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*A*42, 3991 (1990).

6. R.D. Levine
   The Steric Effect in Surface Scattering of Oriented Molecules: An Optical Model Interpretation, *Chem. Phys. Lett.* **174**, 1 (1990).
7. J.I. Brauman, R.N. Zare and R.D. Levine
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8. J.C. Lorquet, Y.M. Engel and R.D. Levine
   On the Separation of Time Scales in the Exploration of Phase Space of an Isolated Molecule, *Chem. Phys. Lett.* **175**, 461 (1990).
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    The Maximum Entropy of an Optical Spectrum and the Redistribution in Phase Space, *Chem. Phys. Letts.* **181**, 307 (1991).
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    Optical Model Computations of Dissociative Chemisorption *J. Phys. Chem.* **95**, 8279 (1991).
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    Mode Selective Chemistry, in: *Mode Selective Chemistry*, B. Pullman, J. Jortner and R.D. Levine, eds., Reidel, Dordrecht (1991), pp. 535-571. Chem. Phys. Letts. **181**, 307 (1991).
19. R.D. Levine and J.L. Kinsey
    On the Repulsion of Energy Eigenstates in the Time Domain, *Proc. Nat'l Acad. Sci. US* **88**, 11133 (1991).
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    The Sequential Exploration of Phase Space in Selectively Excited Polyatomic Molecules, *J. Chem. Phys.*
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    The Determination of Cross-Correlation Functions by Inversion of Raman Excitation Profiles, *Chem. Phys. Letts.*
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    Generating the Spectrum of Nonlinear Hamiltonians,
29. K. Someda and R.D. Levine
    A Generalized Langevin Equation for Wave Functions: A Stochastic Process of Probability Amplitudes
30. Th.D. Sewell, C.C. Chambers, D.L. Thompson and R.D. Levine
    Power Spectral Study of the Classical Vibrational Dynamics of RDX,
31. F. Iachello and R.D. Levine
    Algebraic Theory of Molecules, Oxford University Press (1993).

Appendix A:

ALGEBRAIC THEORY OF MOLECULES

This appendix consists of the introduction and the concluding chapter from a book of this title (by F. Iachello and R.D. Levine) which will be published in 1993 by Oxford University Press.

The entire ms., which is over 500 pages, is available upon request.

INTRODUCTION

Molecular spectroscopy is undergoing an essential change. Seemingly the change is only quantitative; better initial state preparation, improved light sources and specially designed pumping schemes and more sensitive detection techniques are providing ever improved resolution and a wider range of accessible final states, Figure 1.

Figure 0.1. Stimulated emission pumping (SEP, Hamilton et al., 1986; Northrup and Sears, 1992) is a new experimental technique for accessing higher lying vibrational levels of molecules in their ground electronic states. Shown is the SEP vibrational spectrum of SO_2 where a pair of dips represent one vibrational level. (Adapted from Yamanouchi, Takeuchi and Tsuchiya, 1990). The stick spectrum at the bottom represents the position of the vibrational levels given by Equation 0.1 with the constants given in Table 0.1. The bright levels are represnted by longer sticks.

A closer examination suggests also a qualitative change. New ideas and not only better results are forthcoming. One example of the changing attitudes is the increasing concern with time evolution. The time - energy uncertainty relation and the pursuit of higher resolution means that traditional spectroscopy implicitly is equivalent to the study of the stationary states determined by the long time limit of the intramolecular dynamics. The recent increasing concern with the role of anharmonicities and of resonance couplings, made unavoidable by the study of higher lying rovibrational states and the experimental reality of avoiding inhomogenous broadening (e.g., using supersonic expansion, Quack, 1990) make the entire time domain of direct interest to spectroscopists (Bitto and Huber, 1992). The very complementarity with the studies in the frequency domain (broad homogeneous spectral features ≡ early time dynamics and vice versa) makes lower resolution spectra of interest. On the other hand, the traditional concerns of spectroscopy (Herzberg, 1945,1950; Barrow, 1962; King, 1964; Hollenberg, 1970; Herzberg, 1971; Bunker, 1979; Steinfeld, 1985) remain very much with us, Figure 0.2.

Figure 0.2. Direct overtone spectroscopy of C_2H_2 using Fourier transform spectroscopy. Here, at high resolution, the entire band of rotational transitions, which accompany a given vibrational transition, can be resolved. Here the band, in the visible range, corresponding to the direct excitation of $v=5$ of the v_3 stretch mode is shown. (Adapted from Herman et al., 1991. See also Scherer, Lehmann and Klemperer, 1983 and Figure 8.4).

Better determination of overtone and combination bands of familiar molecules and the spectroscopic characterization of new species (radicals (Shida, 1991; Bernath, 1990), ions (Miller and Bondybey, 1983; Leach, 1980) and van der Waals molecules in particular, Nesbitt, 1988; Saykally, 1989; Hutson, 1990; Heaven, 1992) continue to receive wide attention, Figure 0.3.

Figure 0.3. The structure of the van der Waals molecule $C_6H_6 \cdot Ar$ as determined by very high resolution spectroscopy. (Adapted from Weber, van Bargen, Riedle and Neusser, 1990). The potential along the $C_6H_6 - Ar$ stretch motion is shown in Figure 1.4.

What is needed for modern spectroscopy is a formalism able to discuss both level structure beyond the harmonic limit and the corresponding dynamics. A Hamiltonian is thus unavoidable for it is the generator of time evolution. Yet there needs to be a practical method for the determination of the eigenvalues of this Hamiltonian. As in the traditional Dunham-like expansion, it will be useful if the spectra can be well-approximated by a small number of constants. An example of such an expansion is the fit of the vibration spectrum of SO_2 in its electronic ground state, Figure 0.1, by the expansion

$$G(v_1, v_2, v_3) = \sum_i \omega_i(v_i + 1/2) + \sum_{i \le j} x_{ij}(v_i + 1/2)(v_j + 1/2) \qquad (0.1)$$

$$+ \sum_{i \le j \le k} y_{ijk}(v_i + 1/2)(v_j + 1/2)(v_k + 1/2) \; ,$$

Here $G(v_1, v_2, v_3)$ is the level energy in wave number units (as far as possible we follow the notation of Herzberg, 1950) and the constants in Equation 0.1 are given in Table 0.1.

Table 0.1. Vibrational constants[a] (cm^{-1}) for the ground electronic state of SO_2

ω_1	1167.84(15)	y_{111}	-0.0061(10)
ω_2	522.21(19)	y_{222}	-0.0014(18)
ω_3	1382.18(50)	y_{333}	-0.031(22)
x_{11}	-3.655(23)	y_{112}	-0.0001(17)
x_{22}	-0.374(36)	y_{113}	-0.1574(41)
x_{33}	-5.36(20)	y_{122}	-0.0063(19)
x_{12}	-3.129(29)	y_{123}	-0.0509(53)
x_{13}	-14.277(71)	y_{133}	0.255(11)
x_{23}	-4.122(8)	y_{223}	0.0214(50)
		y_{233}	-0.008(12)

[a] A number in parentheses represents a standard error obtained by the least-squares analysis. The vibrational constants, ω_i, x_{ij}, and y_{ij}, are the expansion coefficients of Eq. (0.1). Adapted from Yamagouchi, Takeuchi and Tsuchiya, 1990.

As usual the v's are the vibrational quantum numbers of SO_2 and rather high (above 10) values can be reached using the SEP technique. Eq. (0.1) provides a fit to the observed levels to within an error below 10 cm^{-1} which is almost the experimental accuracy. We need however to be able to relate the parameters in this expansion directly to a Hamiltonian. The familiar way of doing this proceeds in two steps. First, the electronic problem is solved, in the Born-Oppenheimer approximation, leading to the potential for the motion of the nuclei. Then the Schrödinger equation for the eigenvalues of this potential is solved. Since for any but diatomic molecules, the potential is a function of many coordinates, neither the first nor the second steps are simple to implement. For a number of test cases this procedure has been carried out and for diatomic molecules of lower rows atoms it can challenge experiment in its precision. For larger molecules it is still not practical to compute the required potential with sufficient accuracy. It is therefore often approximated using convenient functional forms. Not too far from a deep equilibrium point, the potential can be expanded in the displacements coordinates relative to the equilibrium configuration. Such a 'force field' representation is quite convenient but is of limited validity for higher lying states due to the slow convergence of such a power-series expansion. More flexible functional forms that can describe the asymptotic dissociation plateaux (Murrell et al., 1984) require many parameters. The purely numerical solution of the Schrödinger differential equation for the eigenvalues of such a potential makes the optimization of the parameters in the potential, via a fit to the observed spectrum, a large scale numerical problem complicated, as all such non-linear problems are, by non uniqueness and by local minima.

In this book we present an alternative approach. Our discussion in this introductory volume will put particular emphasis on the traditional concerns, namely determing the levels and intensities of the corresponding transitions. The approach we present retains, at least in part, the simplicity of a Dunham-like approach in that, at least approxiately, it provides the energy as an analytic function of the quantum numbers as in Eq. (0.1). If this approximation is not sufficient, the method provides corrections derived in a systematic fashion. On the other hand, the method starts with a Hamiltonian so that one obtains not only eigenvalues but also eigenfunctions. It is for this reason that it can provide intensities and other matrix elements.

The Hamiltonian used in our approach is an algebraic one and so are all the operations in the method. This unlike the more familiar differential operators of wave mechanics. The technical advantage of an algebraic approach is the comparative ease of algebraic operations. Equally important however is the result, obtained by comparison with experiment, that there are generic forms of algebraic Hamiltonians and that entire classes of molecules can be described by a common Hamiltonian where only the (typically, linear) parameters are different for the different molecules.

The algebraic (or matrix) formulation of quantum mechanics, footnote 1, is less familiar than the differential (or wave) formulation. This is a disadvantage and one purpose of the present volume is to show, by explicit examples, the benefits of the algebraic approach. The interested reader will have to judge if the benefits are sufficient to overcome the potential barrier to the understanding of a new approach. We intend to demonstrate that the algebraic formulation is indeed a viable alternative.

The algebras one uses are Lie algebras. These algebras were introduced at the end of the 19th Century by Lie but it is only in the much more recent past, footnote 2, that they are being used in physics. In the approach that we follow, emphasis is put on starting with the Hamiltonian and the main technical tool is the algebra rather than on the corresponding group. In the appendices to this book, we give an account of the important properties of Lie algebras that are of interest for the applications in the study of molecules, footnote 3.

Even if one restricts attention to vibrations and rotations of molecules, there are a variety of Lie algebras that one can use. In some applications, the algebras associated with the harmonic oscillator are used. We mention these briefly in Chapter 1. We prefer however already in zeroth order to use algebras associated with anharmonic oscillators. Since an understanding of the algebraic methods requires a comparison with more traditional methods, we present in several parts of the book a direct comparison with both the Dunham expansion and the solution of the Schrödinger equation.

In this book we shall write the Hamiltonian as an (algebraic) operator using the appropriate Lie algebra. We intend to illustrate by many applications what we mean by this cryptic statement. It is important to already emphasize that one way to represent such a Hamiltonian is as a matrix. In this connection we draw attention to one important area of spectroscopy, that of electronically excited states of larger molecules, footnote 4, which is traditionally discussed in terms of matrix Hamiltonians the simplest of which is the, so called, picket fence model (Bixon and Jortner 1968). A central issue in this area of spectroscopy is the time evolution of an initially prepared non stationary states. We defer a detailed discussed of such topics to a sequel volume which deals with the algebraic approach to dynamics.

In this book we deal mainly with stationary states, their energies and matrix elements. Unless otherwise stated, we use the wave number (cm^{-1}) as a measure of the energy. The conversion factors with other units are shown in Table 0.2.

Table 0.2. Energy conversion factors[a)]

Unit	cm^{-1}	eV	Hz(sec^{-1})	J/mole	°K
1 cm^{-1}	1	1.2398(-4)	2.997924(10)	1.1962(1)	1.4388
1 eV	8.06573(3)	1	2.41804(14)	9.6487(4)	1.16049(4)
1 Hz(sec^{-1})	3.3356(-11)	4.1356(-15)	1	3.9903(-10)	4.7993(-11)
1 cal/mole	0.34976	4.3363(-5)	1.04854(10)	4.1840	0.50325
1°K	0.69503	8.6170(-5)	2.0836(10)	8.1340	1

[a)] The numbers in parentheses represent powers of ten.

$1Å = 10^{-8}$ cm $= 0.1$ nm $= 10^{-4}$ μm $= 10^{8}/(cm^{-1})$. Speed of light in vacuum $c = 2.99792458 \times 10^{8}$ $msec^{-1}$. The meter is now defined as the distance traveled by light in vacuum in $1/c$ sec, so that c is a defined constant and the second (as measured by atomic clocks) is the fundamental unit. The cal is still an often used energy unit. For a complete account, see Mills (1988).

The present volume deals exclusively with rotation-vibration spectra. Electronic excitations can also be described algebraically, but this description is still at a too preliminary stage for inclusion in a book format.

Footnotes

1. The matrix formulation of quantum mechanics was introduced as early as 1925 by Heisenberg, 1925; Born and Jordan, 1925; Dirac, 1925; Born, Heisenberg and Jordan, 1926.

2. It was only in the 1930's that Lie algebras were being used in physics (Weyl, 1931; Wigner, 1931, 1937; van der Waerden, 1931; Yamanouchi, 1937; Racah, 1942, 1949). Most of the early applications dealt with the algebra of rotations (Wigner-Racah algebra). In this volume we aim to present a unified approach which starts from the algebra as the key tool for the construction of spectra and intensities. This approach originated in the 1960's (Dothan, Gell'Mann and Be'eman, 1965; Barot and Böhm, 1965) and had major applications in nuclear physics (Iachello and Arima, 1974; Arima and Iachello, 1975. For an update, see the books by Iachello and Arima, 1987 and Iachello and van Isecker, 1991 and the reviews in Böhm, Ne'eman and Barut, 1988). In our discussion we shall emphasize the role of the algebra rather than that of the corresponding group. Specifically, we shall seek such a description that even in zeroth order the spectrum is anharmonic. We shall also try to forge a clear link with the geometrical point of view. There are many other important applications of Lie groups and algebras. In particular, we do not discuss time dependent aspects (Alhassid and Levine, 1977; Wulfman, 1979; Levine and Wulfman, 1979; Levine, 1985) nor other applications (e.g., Coherent States (Klauder and Skagerstam, 1985; Perelemov, 1986; Zhang et al., 1990) or configuration interaction in electronic structure calculations (Judd, 1968; Paldus, 1978; Hinze, 1981; Pauncz and Matsen, 1986; Adams et al., 1987; Duch, 1988)) where the group structure is of central importance.

3. Lie groups and Lie algebras are discussed in many textbooks (Hamermesh, 1962; Lipkin, 1965; Gilmore, 1974; Wybourne, 1974; Barut and Rqczka, 1986). We follow closely the notation of Wybourne, 1974. There are also a number of mathematical texts (Miller, 1968; Talman, 1968; Vilenkin, 1968; Miller, 1977, Olver, 1986).

4. Hamiltonians expressed in matrix forms have been extensively employed in the theory of radiationless transitions of electronically excited states of larger molecules (Bixon and Jortner, 1968; Schlag et al., 1971; Freed, 1972; Nitzan et al., 1973; Avouris et al., 1978; Jortner and Levine, 1981; Felker and Zewail, 1988; Seel and Domcke, 1991).

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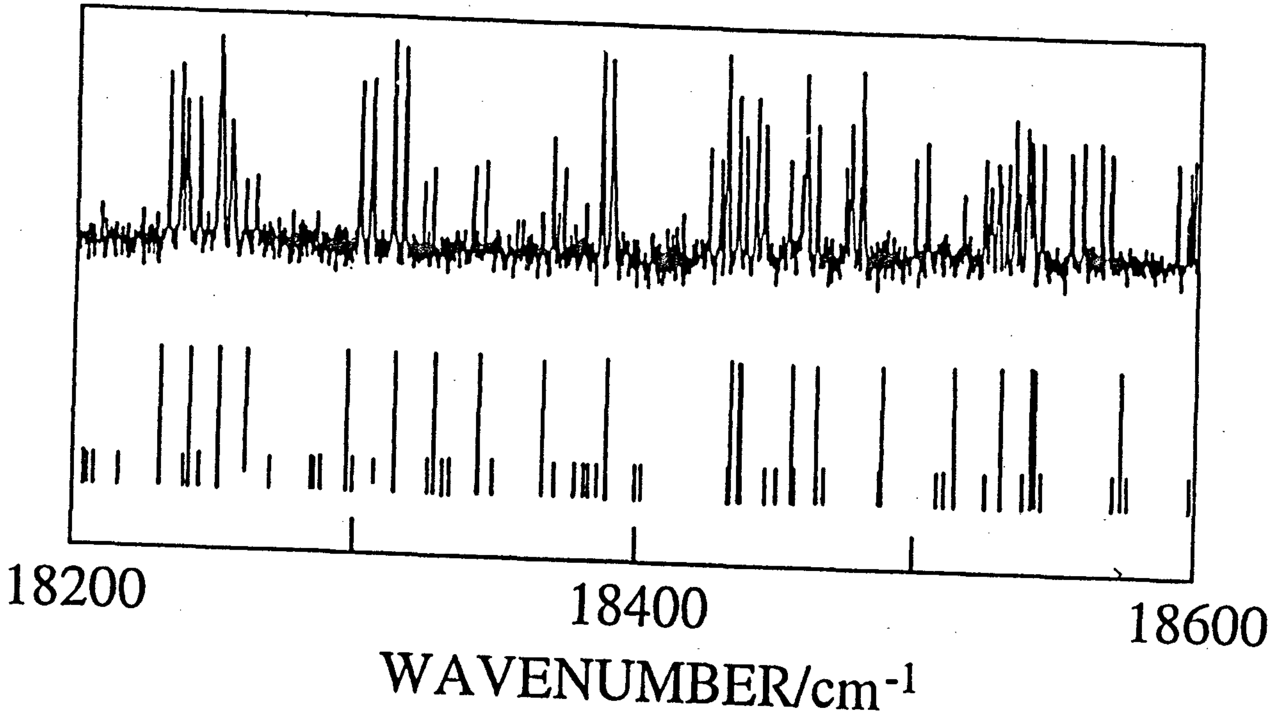
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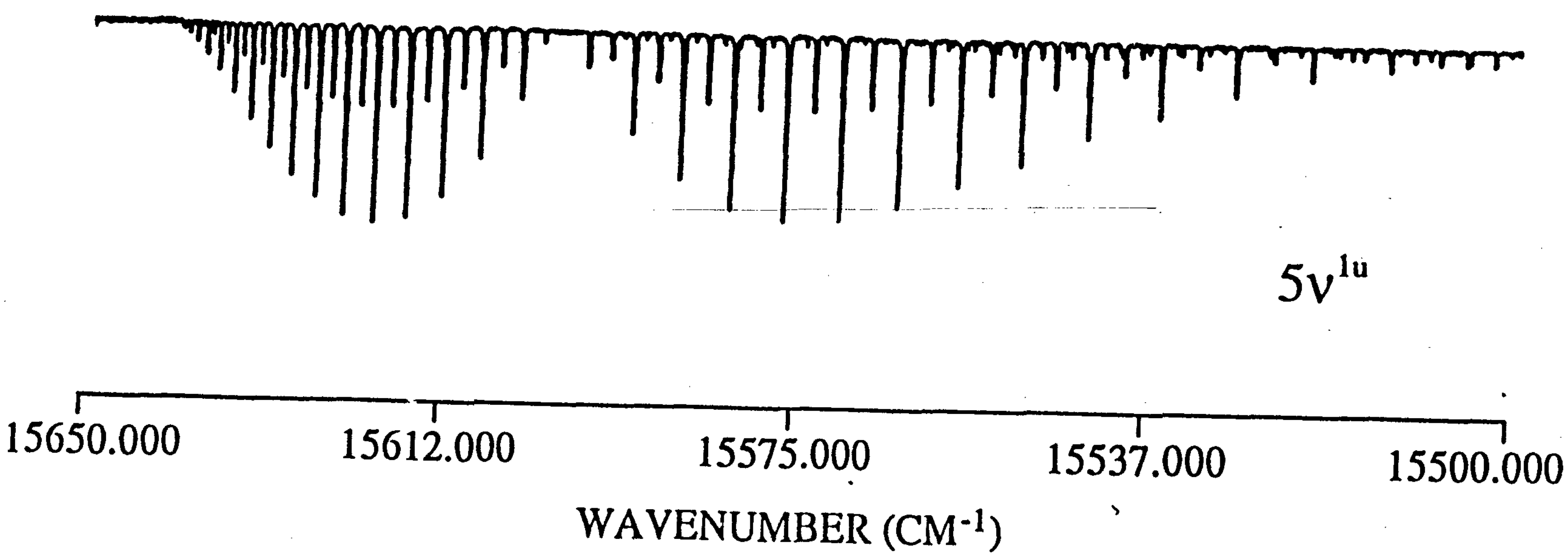
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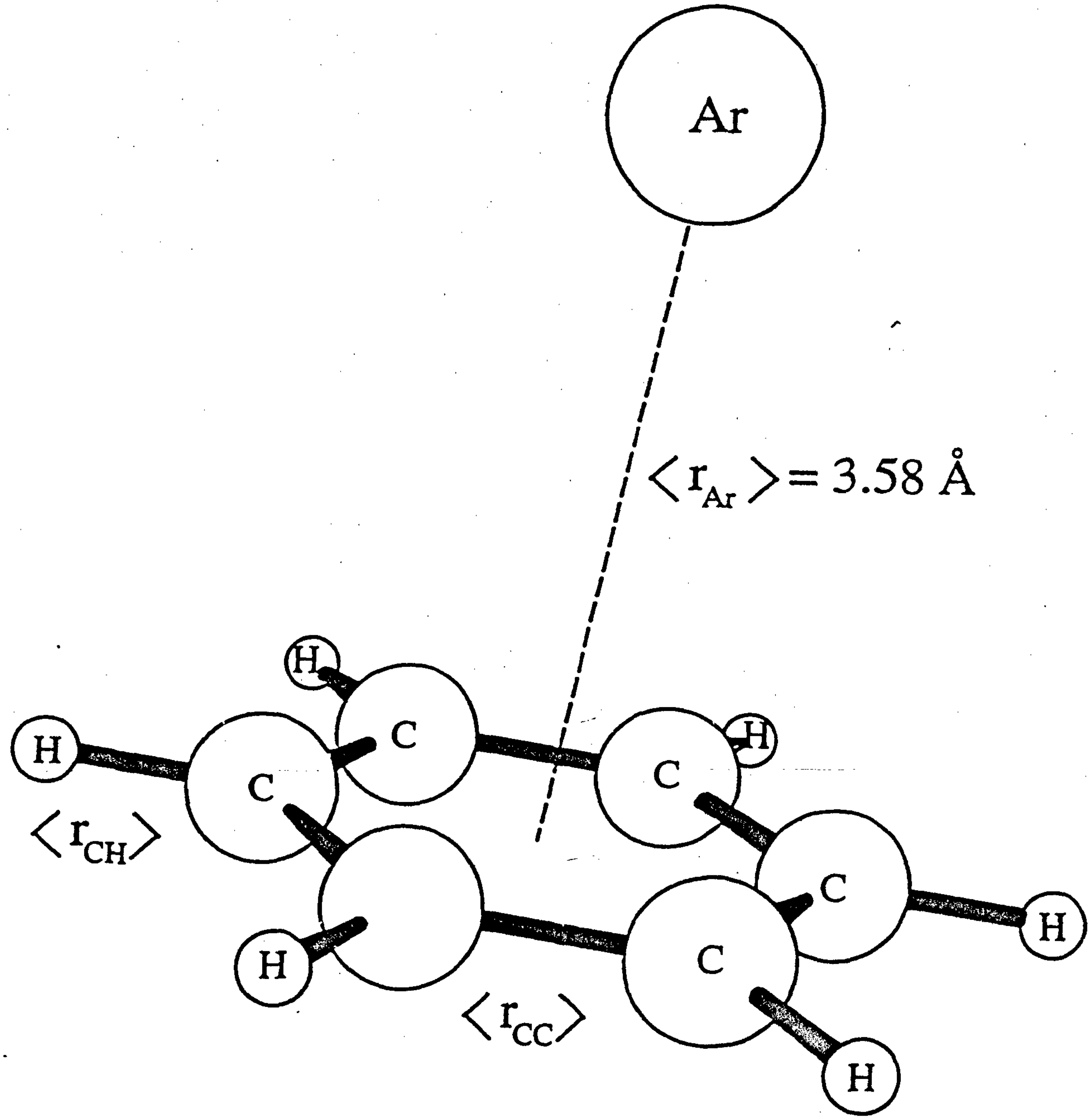
Ar
$\langle r_{Ar} \rangle = 3.58$ Å
H
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C
$\langle r_{CC} \rangle$
H

CHAPTER 8

PROLOGUE TO THE FUTURE

At this point, we hope to have demonstrated that the algebraic approach provides a viable method for the quantitative description of molecular vibrotational spectra. Chapters 5 (triatomic molecules, both linear and bent) and 5 (linear tetratomic molecules) and Appendix C provide extensive documentation for the quantitative applications, while Ch. 6 shows that larger molecules can also be treated. Throughout, but most particularly in Ch. 7, we have sought to forge link with the more familiar geometrical approach. It is precisely our requirement that even in zeroth order the Hamiltonian we start with describes an anharmonic motion, which makes this link not trivial. The advantage of our requirement in providing, even in zeroth order, high overtone spectra which are typically more accurate than 10 cm^{-1}, should not be overlooked. Yet much remains to be done. In this chapter we look to the future: Where and why do we think that the algebraic approach will prove particularly advantageous. Of course, what we really hope for is to be surprised by unexpected new developments and applications. Here, however, is where we are certain that some of the future progress will be made, with special reference to the spectroscopy of higher energy states of molecules.

One area of spectroscopy where the Hamiltonian in matrix form is the route of choice is that of large polyatomics, particularly so when in an electronically excited state, footnote 0.3. Such states are isoenergetic with very high vibrational overtones of the ground electronic states so that a fully geometrical approach is impractical. Even at lower energies, the exceedingly high density of vibrational states strongly favours an alternative approach and the use of model Hamilton matrices is not uncommon. Such model matrices are introduced so as to account for the regularities that often survive in the observed spectrum. One such striking feature is often referred to as a 'clump' (Hamilton et al. 1986). Consider a pure vibrational progression of states as can be observed in stimulated emission spectroscopy, SEP, Figure 0.1. A clump is a spectral feature that appears as a broad line at a given spectral resolution but which is revealed to be a set of overlapping lines when a higher resolution is used. To qualify as a 'clump', the width needs to be inherent rather than instrumental. By inspection of Figure 0.1 one can imagine that the spectrum will exhibit clumps at a lower resolution. It can even be that there are clumps within a clump, Figure 8.1.

Figure 8.1. A spectral clump and its two tiers of fine structure. (The sharp feature at ~8770 cm^{-1} in panel b is the envelope of the set of lines shown in panel c). When states are coupled in a sequential manner there can often be a separation of time scales in the temporal evolution of a non stationary state or a corresponding separation of frequency scales in the spectrum. (Remacle and Levine, 1992). Algebraic Hamiltonians provide a convenient framework for the discussion of sequential coupling.

For small polyatomics (e.g., NO_2, $C_2H_4^+$) one can think of the coupling of different electronic states from a geometric point of view (Englman, 1972 ; Köppel et al., 1984; Whetten et al., 1985). Even then a transformation to a matrix Hamiltonian is typically very useful and is often implemented particularly when only a very limited number (two, three) electronic states are coupled. By using a Hamiltonian expressed in terms of generators for the electronic degrees of freedom one can describe a multistate electronic spectrum (Frank et al., 1986, 1989, 1991; Lemus et al., 1992; Lemus and Frank, 1991, 1992). Moreover, one can couple the electronic motion to anharmonic motion of the nuclei. In the future one can confidently expect to see many more such applications.

An algebraic approach to electronic degrees of freedom will be particularly advantageous when the density of electronic states is high and the coupling to the rovibrational motion is strong. Such is the case for very high Rydberg states which lie just below the ionization continuum. For larger molecules there is a very facile energy exchange between the electronic and nuclear manifold of states. There is currently a revival of interest in such problems (Schlag and Levine, 1992). For smaller molecules (NO, H_2O) the relevant couplings are currently being delineated by spectroscopic techniques (e.g., Bryant et al., 1992; Gilbert and Child, 1991).

Next, we turn to dynamics proper. Spectroscopy itself is intimately related to intramolecular dynamics, that is to the time evolution of a non stationary state of the Hamiltonian. Detailed applications of algebraic methods to such problems have so far been mostly limited to problems where the Hamiltonian is a linear expression in terms of the generators of the algebra. The reason why this is the case can be understood even without an appeal to the group concept: Let X, at time $t = 0$ be a generator whose time evolution $X(t)$ is of interest. Then, in the Heisenberg picture: $i\hbar dX(t)/dt = [X(t), H]$. It follows from the closure property of Lie algebras, Equation 2.1, that if $X(t)$ and H are in the algebra so is the time rate of change of $X(t)$ and therefore so is $X(t + dt)$. Hence, if X at $t = 0$ is an operator in the algebra and the Hamiltonian is any linear combination of generators, $X(t)$ remains in the algebra. A key open problem, footnote 1, is how to proceed in the more realistic case when the Hamiltonian is bilinear rather than linear in the generators of the algebra.

The second set of problems in dynamics are those of scattering theory where the Hamiltonian is of the form $H = H_0 + V$ and the interaction V vanishes when the colliding particles are far apart. It is usually assumed that the H_0 part is already solved and that the interesting or the hard part is to account for the role of V. For realistic systems which are anharmonic even the role of H_0 can be quite significant. An example which received much recent attention is the reaction of vibrationally excited HOD with H atoms (Sinha et al., 1991), Figure 8.2.

Figure 8.2. Schematic illustration of the preferential reactivity of HOD with an H atom when the stretch excitation is localized in either one of the two bonds.

The large difference in the OH and OD vibrational frequencies means that the stretch overtones of HOD are primarily local in character, cf. Section 4.21. It follows that one can excite HOD to overtones localized preferentially on either one of the two bonds and that an approaching H atom will abstract, preferentially either an H or a D atom, Figure 8.2. Even in the lowest stretch states this selectivity is maintained (Bronikowski et al., 1991).

As in scattering theory in general, one can treat the role of V in either a time independent or a time dependent point of view. The latter is simpler if the perturbation V is either explicitly time dependent or can be approximated as such, say by replacing the approach motion during the collision by a classical path. Algebraic methods have been particularly useful in that context, footnote 2, where an important aspect is the description of a realistic level structure for H_0. Figure 8.3 is a very recent application to electron-molecule scattering.

Figure 8.3. The vibrational elastic and inelastic differential cross sections for electron scattering off LiF at E=5.44 eV. (Alhassid and Shao, 1992). Solid lines: with an improved dipole interaction (which breaks the $O(4)$ symmetry). Long dashed lines: the calculations by Bijker and Amado (1986). The short dashed lines are the Born approximation.

In time dependent collision theory, the asymptotic states 'after' or 'before' the collision are defined by the limits of $t \rightarrow \pm\infty$. In time independent theory one can either use a Lippmann-Schwinger like approach (Alhassid and Levine, 1985) or define scattering through a coordinate representation (Alhassid et al., 1983, 1984, 1986; Ojha, 1986; Wu et al., 1987, 1989; Frank and Wolf, 1984; Frank et al., 1986, 1985). The latter has been more extensively studied, since for scattering by a potential the geometrical connection is well understood, cf. Chapter 7. Applications to systems with internal structure (e.g., Wehrhahn, 1990, 1991; Wehrhahn and Levine, 1991) are still in their early stages.

In its initial stage of development, the algebraic approach has sought to show why and how it provides a framework for the understanding of large amplitude, anharmonic motion. Much of our concern in this volume has been with this stage including, of course, the even simpler problem of uncoupled motions. In its current stage the approach will seek to keep pace with the new developments of modern spectroscopy including the interest in floppy molecules. The better understanding of the overtones of polyatomics including the higher energy regimes where the non rigidity is sufficient to allow for isomerization will, no doubt, continue to be of central concern. This will include not only vibration-rotation coupling but also rovibration-electronic coupling. In terms of the connection to the geometrical picture this means, of course, that one is interested in the shape of the potential further and further away from its global minimum and, in particular, in the possibility of local minima. Moreover, at increasing coupling, the very concept of the potential becomes less useful. The algebraic approach offers a special advantage under such circumstances.

At higher light intensities, it is no longer possible to treat the coupling to the field in lowest order in perturbation theory (George et al., 1977) and algebraic techniques again become particularly useful. The emphasis of a time domain interpretation of spectroscopy is very likely to further increase. This is not only because of spectroscopic experiments in the time domain (Khundkar and Zewail, 1990; Pollard and Mathies, 1992) but also because of the 'time window' which is revealed by experiments in the frequency domain (Imre et al., 1984), a time window which covers the very range of interest to chemists. The emphasis on the time domain has also revived the interest in coherence effects in optical spectroscopy (Steinfeld, 1985). Then there are larger molecules up to and including molecules of biological interest, clusters, etc. One has both experimental and theoretical reasons to expect that increasing the size does not necessarily imply an exponential increase in the complexity and unwieldiness of the spectrum, Figure 8.4.

Figure 8.4. The $\nu = 6$ CH overtone spectrum as determined by photoacoustic absorption (Hall, 1984) for increasing size alkynes. Each panel contains the

molecular formula and the density of vibrational states per cm^{-1}. The band origin does shift some with size but is roughly at 18450 cm^{-1} for all the molecules shown. (See also Kerstel et al., 1991).

Finally, one expects spectroscopy to have an increasing impact not only on intramolecular but also on intermolecular dynamics. This includes not only a better understanding of the reactants, as in Figure 8.2, but also the application of spectroscopy to the very collision process (Brooks, 1988; Neumark, 1992). At lower light intensities, spectroscopy acts in its usual role as a probe except that it is probing very transitory events. At higher intensities one can guide and not only monitor the evolution of the system (Jortner et al., 1991; Rabitz and Shi 1991; Rice, 1992; Brumer and Shapiro, 1992). The discussion of control of quantum systems is one more area to which algebraic techniques can and will usefully contribute.

Footnotes

1. The problem of time evolution for a Hamiltonian bilinear in the generators (Levine, 1982) has been extensively discussed. The proposed solutions include the use of variational principles (Tishby and Levine, 1984), mean field self consistent methods (Meyer et al., 1988), time dependent constants of the motion (Levine, 1982) and numerous others which we hope to discuss in detail in a sequel to this volume.

2. Algebraic methods have been effectively employed in time dependent collision theory (Alhassid and Levine, 1977, 1978). In the sudden approximation (Levine and Wulfman, 1979) and the use of an H_0 which is bilinear in the generators presents no real problems. This has been very effectively employed in electron-molecule scattering (Bijker et al., 1986, 1988, 1990; Ginocchio et al., 1986; Mengoni and Shirai, 1988, 1991; Alhassid et al., 1993), where due to the high velocity of the incident electron one can neglect the change in its path due to energy transfer to the molecule.

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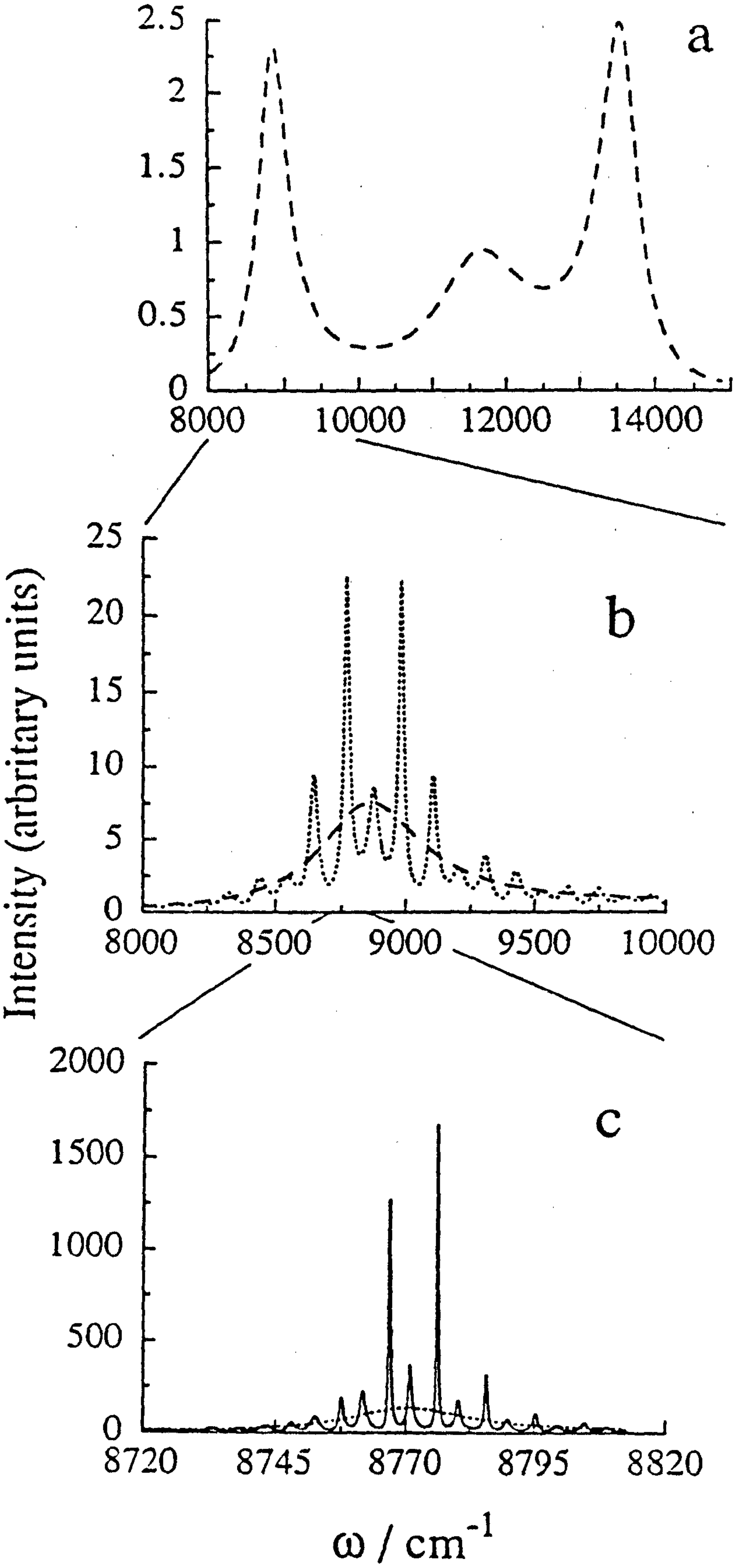
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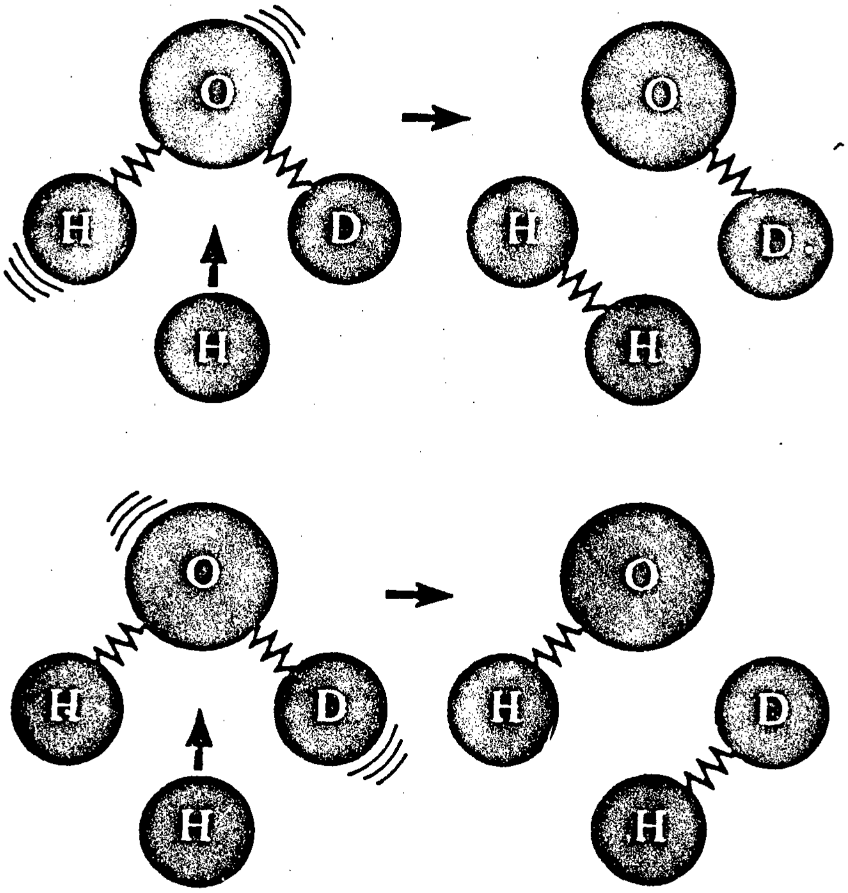
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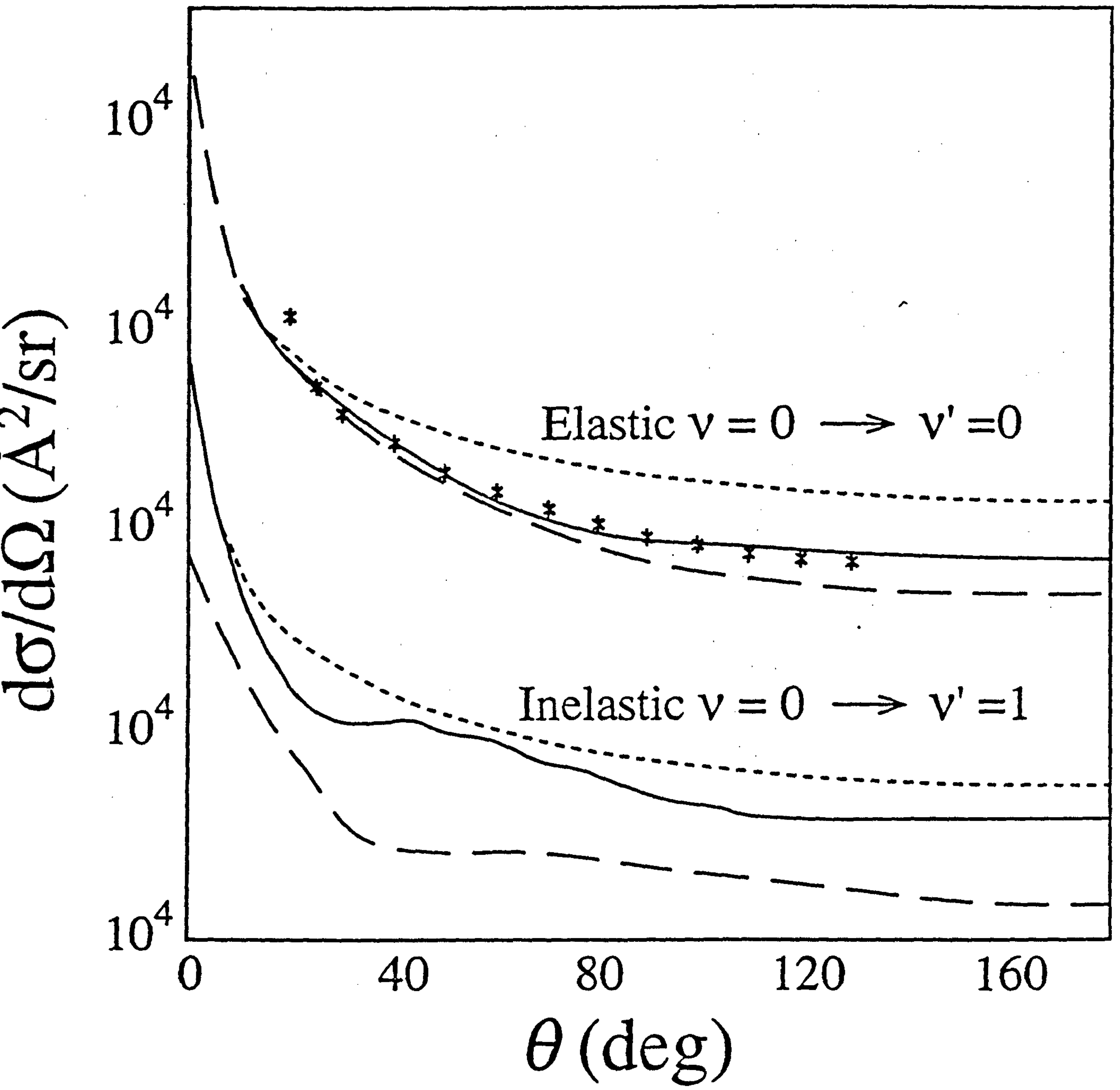
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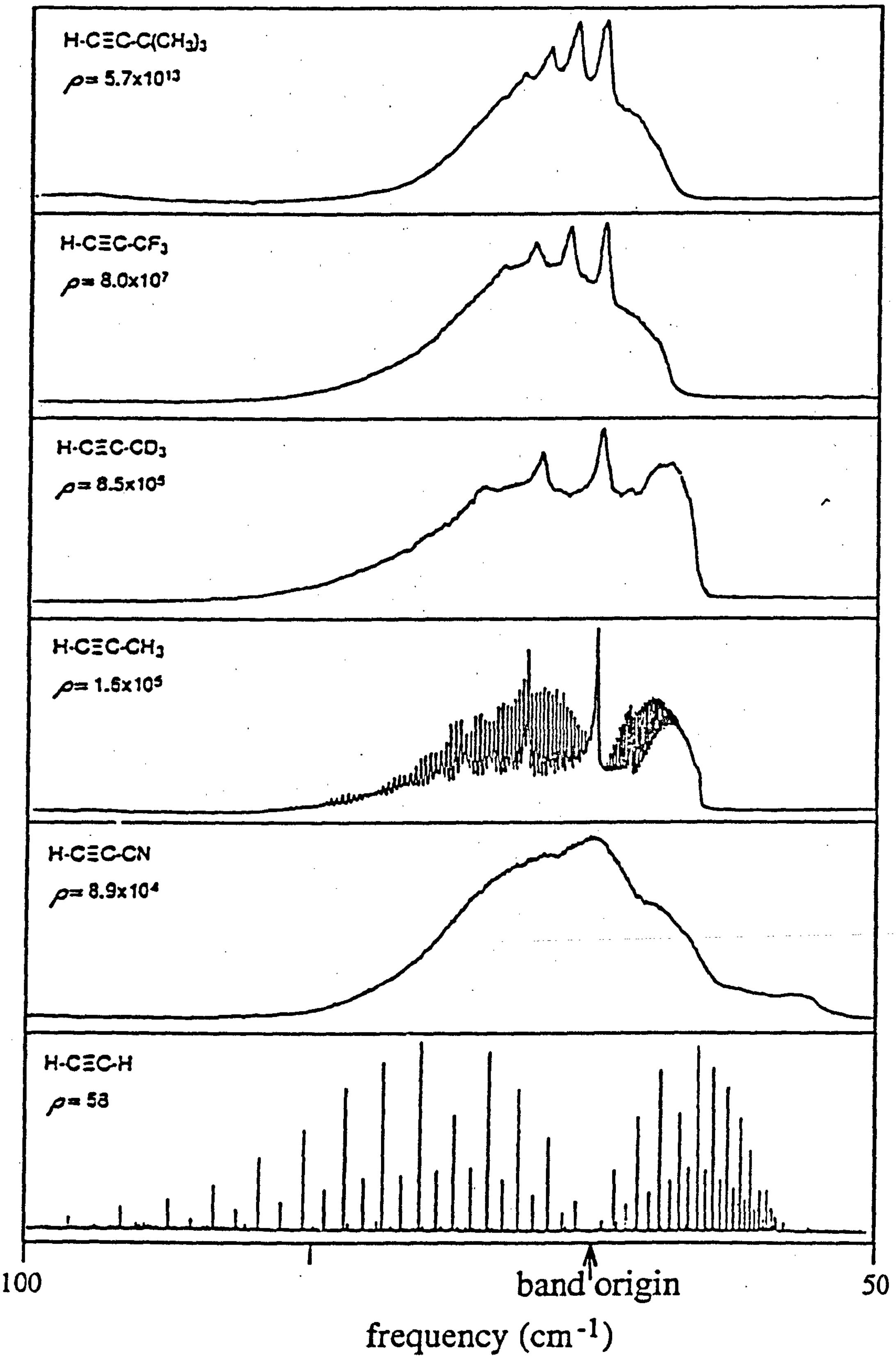
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ρ= 5.7x10^13
H-C≡C-CF3
ρ= 8.0x10^7
H-C≡C-CD3
ρ= 8.5x10^5
H-C≡C-CH3
ρ= 1.6x10^5
H-C≡C-CN
ρ= 8.9x10^4
H-C≡C-H
ρ= 58
-100
band origin
50
frequency (cm-1)

Appendix B:

THE DETERMINATION OF TIME CROSSCORRELATION FUNCTIONS BY INVERSION OF RAMAN EXCITATION PROFILES

This appendix is the entire text of the short paper, with the above title, by F. Remacle, R.D. Levine and J.L. Kinsey.

A much more detailed version is also ready for publication.

The Determination of Time Crosscorrelation Functions by Inversion of Raman Excitation Profiles

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The short time dynamics of a nonstationary state is here determined by a direct inversion of an experimentally measurable Raman excitation profile. The procedure is based on the analytic properties of the Raman scattering amplitude and is best implemented within the maximum entropy formalism. A computational example for resonance Raman excitation profiles in the B state of iodobenzene is presented.

PACS numbers: 33.10.Cs, 33.20.Fb, 02.70.+d, 33.70.-w

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Rabinovitch and coworkers. Chemical clocking[5,11,12] in particular provides striking evidence for exceedingly fast delocalization. Some of the reported rates are just an order of magnitude slower than typical vibrational frequencies.

Our question is whether the loss of the selectivity of the initial excitation, in highly excited molecules, is indeed so rapid. We shall bring forth arguments in support of a much more gradual and sequential loss. In particular we shall argue that the rapid sub-ps initial stage will have the same temporal character in a purely harmonic molecule. At the end of this first stage the molecule has by far not sampled the majority of its energetically accessible phase space. Hence we shall conclude that the fast initial dephasing is definitely not sufficient to establish the representative coverage of phase space which is assumed in the RRKM approach.

The reason for reexamining this question are the recent high resolution spectroscopic experiments of higher overtones of polyatomic molecules[12–20]. Adopting a time dependent point of view[21,22] such high resolution experiments provide insight on the temporal evolution of the initially localized excitation[22–30]. These, and the corresponding studies in the frequency domain[31–36] furnish what, from the standpoint of chemical kinetics, is complementary the short time information.

The information provided by both collisional clocking and the inversion of spectroscopic data is essentially indirect information. Ultimately, real time monitoring[37–40] will allow a direct probe of the dissociation process. For the time being, overtone spectroscopy provides useful insights on the first dozen ps or so following the $t = 0$ initiation of a non stationary molecular state. It would be of considerable interest to extend the time domain into the sub-ns range. This however is unlikely to be realized in the immediate future. Such time intervals are long on the spectroscopic scale as they require a frequency resolution which is typically unrealistic at the high excitation energies of interest. Computations are equally better at shorter times, for both numerical reasons and for the need to know finer and finer details of the Hamiltonian in order to obtain a higher resolution spectrum or, equivalently, an accurate longer time propagation.

THE EXPLORATION OF PHASE SPACE

Of the many possible spectroscopic techniques we here select for discussion the two that most readily correspond to the information of interest. The normalized absorption spectrum $S(\omega)$ [22] and the normalized resonant Raman excitation spectrum $\sigma(\omega)$[41,42]. (Note that there are other Raman cross sections, most notably the Raman emission cross section, which is not here discussed). The two types of spectra are related to two time correlation functions. The absorption spectrum is the Fourier transform of the time autocorrelation function $C(t)$ of an initial non-stationary state $\phi(0)$

$$C(t) = \int \exp(-i\omega t) S(\omega) d\omega$$

$$C(t) = <\phi(0)|\phi(t)> \ .$$

The spectral intensity p_n, at the energy of the n'th eigenstate ψ_n,

$$S(\omega) = \sum_n p_n \delta(\omega - \omega_n) \ ,$$

is related to $\phi(0)$ by

$$p_n = | <\psi_n|\phi(0)> |^2 \ .$$

The time autocorrelation function determines the 'survival probability', $|C(t)|^2$ of the non stationary state, $|C(t)|^2 = | <\phi(t)|\phi(0)> |^2$.

It is equally of interest to determine not only where the initial state is not, but where it is. This information is provided by the time crosscorrelation function $<\phi_f(0)|\phi_i(t)>$ which is related to the resonant Raman excitation cross section

$$\sigma_{fi}(\omega) = \left| \int_0^\infty <\phi_f|\phi_i(t)> \exp(i\omega t)dt \right|^2 \ .$$

Note however that unlike $S(\omega)$ and $C(t)$ which are a Fourier transform pair, the time cross correlation function determines the Raman excitation cross section but the inversion of this relation is less immediate. The direct route is thus to compute the time crosscorrelation function from the dynamics and to obtain the excitation profile as the one-sided Fourier transform. Recently we have however developed a method of analysis for extracting the time crosscorrelation function from the Raman excitation profile. $C(t)$ on the other hand can either be computed or determined directly from the experimental data, figure 1.

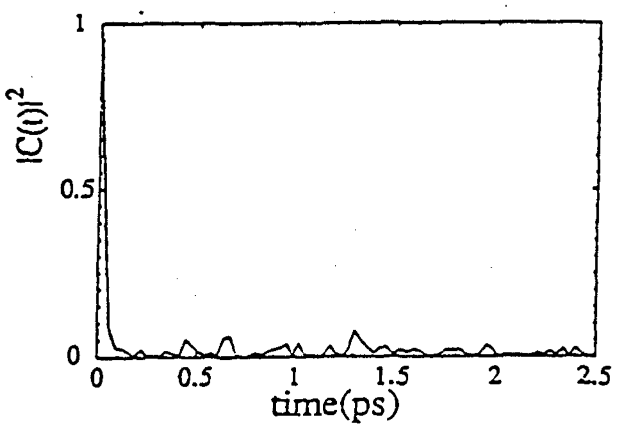

Figure 1. The survival probability $|C(t)|^2$ determined by a Fourier transform of the excitation spectrum of acetone in the visible and near UV. High resolution experimental data of H. Zuckermann, Y. Haas, M. Drabbels, J. Heinze, L. Meerts, J. Reuss, and J. van Bladel.

The short time evolution of $C(t)$ has been extensively discussed[22-30]. In particular, considerable attention was given to the notion of the correlation hole[15,19,28,29,43]. Here, however, we draw attention to a much more prominent feature, namely the very rapid drop of $|C(t)|^2$ from an initial value of unity to an (average) value smaller by one or more orders of magnitude, figure 1. The point is that this drop occurs on a time scale of vibrational periods and does not provide evidence for intramolecular vibrational energy redistribution. In other words, consider two Hamiltonians H_0 (whose spectrum is regular) and $H = H_0 + V$ where V includes the diverse anharmonic couplings. While V will cause local level repulsions, splittings, etc., the envelope of the spectrum of H_0 and H will be essentially identical. Since the gross structure in $S(\omega)$ is the same, the short time dependence of $C(t)$ will be the same.

That the initial time evolution does not discern the fine spectral details (which indicate the presence or absence of chaos) is not a uniquely quantal phenomena. It can just as well be understood on purely classical considerations. For historical reasons we phrase the discussion in terms of Slater's model of unimolecular dissociation[44]. Recall that in the Slater model the molecule is perfectly harmonic. The extension of the bond to be broken is written as a linear superposition of normal modes. Each mode with its own phase, which varies with time in accord with its harmonic frequency. As the phases vary, so does the extension of the bond to be broken. Dissociation is said to take place when, due to a phase matching, the bond is extended to a critical value. Now let us run this mechanical system backwards in time: An initially extended bond rapidly returns to a more average value due to the dephasing of the normal modes, each beating with its own frequency. The analogy with the optical excitation is established by thinking of the initial bond extension as resulting from a vertical Condon transition. The initial drop of $|C(t)|^2$ corresponds to the Slater-like dephasing process of the non-interacting modes.

In a purely harmonic Slater-type model, the initial dephasing leading to the contraction of the extended bond will eventually lead to a rephasing and an elongation of the bond. There is however an important proviso since real molecules are anharmonic. $|C(t)|^2$ does not recur back to its initial value of unity but to a lower value. It is this, much more gradual, relaxation of $|C(t)|^2$ which reflects the sampling of phase space. The same is true for a quantal time evolution.

ANALYSIS OF SEQUENTIAL EVOLUTION IN PHASE SPACE

The molecular eigenstates provide one suitable basis for discussing the time evolution of $C(t)$. In that basis the time history is entirely expressed in terms of dephasing since the eigenstates themselves are stationary

$$C(t) = \sum_n p_n \exp(-iE_n t/\hbar) \quad .$$

It is the distribution of the intensities, p_m, and the spacings $E_n - E_m$, as reflected in the spectral autocorrelation function $G(\omega)$, the so called 'power spectrum'[23]

$$|C(t)|^2 = \int d\omega \exp(-i\omega t) G(\omega)$$

$$G(\omega) = \sum_n \sum_m p_n p_m \delta(\omega_n - \omega_m - \omega)$$

that determines the different time regimes in $|C(t)|^2$ if such regimes exist.

$G(\omega)$ is the weighted distribution (by $p_n p_m$) of spacings in the spectrum. Note that $G(\omega)$ describes not only the distribution of spacings[45] but also the fluctuation of intensities.[46] Our understanding of molecular spectra is sufficient for us to recognize that $G(\omega)$ may well contain several peaks. The one at highest spacings (or shortest times) corresponds to spacings of different vibrational states. Next are contributions from the dominant anharmonicities (the largest resonant couplings), etc. One sees very clearly the existence of several scales in $G(\omega)$ for spectra taken at different resolutions (sometimes referred to as 'clumps', see, e.g. Refs. 15,18,47). At each increasing scale there is a new set of lines, which merge into a clump when the resolution is reduced, figure 2.

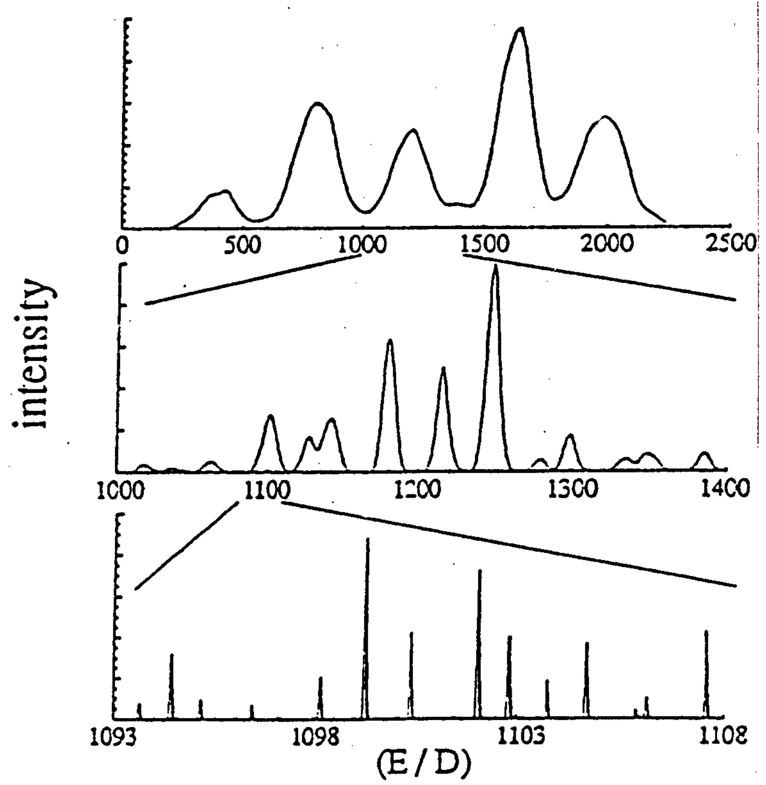

Figure 2. A (computed) spectrum at three levels of resolution, plotted vs. the frequency measured in units of the mean spacings between eigenstates. A group of resolved lines at the highest resolution (bottom panel) appears as a single feature (a 'clump') at a lower resolution. A group of clumps appears as a single clump at the lowest resolution (uppermost panel).

The nested structure of the observed spectrum suggests that it may be useful to consider an alternative basis set, corresponding to a zeroth order Hamiltonian H_0. The initially excited optically 'bright' states correspond to a small subset of states of H_0. Elsewhere[48] we have discussed the nested structure of the perturbation, V, $V = V_1 + V_2 + \cdots$, which gives rise to a sequence of Hamiltonians H_i, $H_1 = H_0 + V_1$, $H_2 = H_1 + V_2, \ldots$, such that it is the eigenstates of H_i which span the phase space sampled by the i'th stage. In terms of the eigenstates of H_0, each stage corresponds to a larger subset of states which are coupled to the initially prepared state. One can therefore define projection operators M_i, which project onto the subspace of states of H_0 relevant at the i'th stage, such that

$$M_i = M_{i-1} + \bar{M}_i = \sum_{r=0}^{i} \bar{M}_r \quad .$$

Here, $\bar{M}_r$ is the projection on the new set of states brought into coupling at the r'th stage and $M_0 = \bar{M}_0$.

The experimental observation of a clump structure in the spectrum means that one can compute a survival probability for a given clump. Therefore one can determine from the observed spectrum not only $|C(t)|^2$,

$$|C(t)|^2 = Tr(M_0 \rho(t)) \quad ,$$

where $\rho(t) = |\phi(t)><\phi(t)|$, but also

$$\begin{aligned} |C_i(t)|^2 &= Tr(M_i \rho(t)) \\ &= \sum_i Tr(\bar{M}_i \rho(t)) \quad . \end{aligned}$$

In the maximum entropy approach,[27,48] we determine $\rho(t)$ as the most spread out density subject to the constraints imposed by the spectrum, i.e. the values of the survival probabilities $|C_i(t)|^2$, $i = 0, 1, \ldots$. Taking into consideration that $Tr(\rho(t)) = 1$ and $\bar{M}_{i-1}\,\bar{M}_i = 0$, one obtains for $\rho(t)$

$$\rho(t) = \exp\left(\sum_{r=0}^{R} \mu_r(t) \bar{M}_r\right)/Z$$

where Z insures the normalization of $\rho(t)$

$$Z = Tr\left(\exp\left(\sum_{r=0}^{R} \mu_r(t) \bar{M}_r\right)\right)$$

and R is the highest level of nesting evident in the spectrum, $\bar{M}_{R+1} = I - \sum_{r=0}^{R} \bar{M}_r$ and $\mu_{R+1}(t) \equiv 0$. Two very suggestive forms of $\rho(t)$, obtained using the orthogonality of the $\bar{M}_i$'s are

$$\rho(t) = Z^{-1} \sum_{r=0}^{R+1} \exp[\mu_r(t)] \bar{M}_r$$

showing that $\exp(\mu_r(t))Tr[\bar{M}_r]/Z$ is the fractional occupancy of the r'th subspace and the nested form

$$\rho(t) = Z^{-1}\{\bar{M}_{R+1} + \exp(\lambda_R(t))\{\bar{M}_R + \exp(\lambda_{R-1}(t))\{\bar{M}_{R-1} + \cdots$$
$$+ \exp(\lambda_1(t))\{\bar{M}_1 + \exp(\lambda_0(t))\bar{M}_0\} \cdots\} \ .$$

Here the $\lambda_r(t)$'s are the Lagrange multipliers conjugate to the survival probabilities $|C_r(t)|^2$ and are related to the $\mu_r(t)$'s by

$$\begin{aligned} \lambda_R &= \mu_R \\ \lambda_{R-1} &= \mu_{R-1} - \mu_R \\ &\cdot \\ &\cdot \\ \lambda_0 &= \mu_0 - \mu_1 \end{aligned}$$

A plot of the entropy of $\rho(t)$ for a system manifesting a separation of time scales is shown in figure 3. (The corresponding frequency spectrum is shown in figure 2). A detailed discussion of sequential time evolution is available in Ref. 48. Earlier closely relevant work includes Refs. 26, 27 and 30.

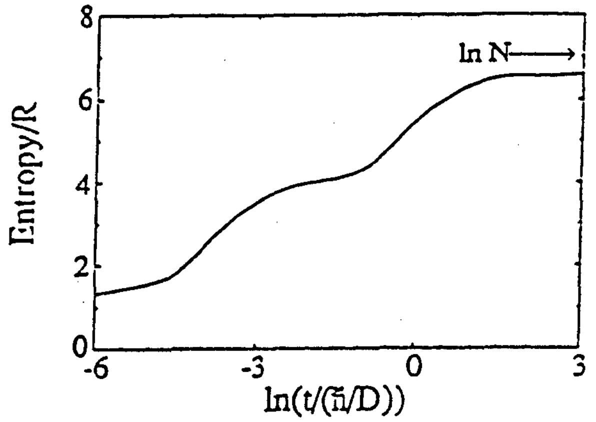

Figure 3. The entropy (in units of R) vs. time (in units of $\hbar$/mean spacings, logarithmic scale) computed for the density in phase space of maximal entropy. The survival probabilities vs. time are those determined by the spectrum shown in figure 2. Note the clear separation into three time regimes (the logarithmic abscissa scale makes it possible to show the different regimes on the same plot). N is the number of eigenstates so that for a strictly uniform covering of phase space the long time value of the entropy should be $R \ln N$. As can be seen the actual asymptotic value is somewhat lower. This is due to the fluctuation of the spectral intensities.[46]

In a wider context, the separation of time scales, as reflected in the sequential evolution stages in phase space, is a particular case of impulsive coupling. Impulsive coupling, manifested in a variety of intramolecular dynamics systems[49] e.g., van der Waals clusters, energy rich molecules, reactions in liquids[50] and on surfaces,[51] is the rather sudden switch from a motion confined to a smaller region of phase space to a less confined mode. It results from terms in the Hamiltonian which are 'non-resonant' on a shorter time scale and thus not included for shorter time dynamics.

DYNAMICS

An alternative to extracting the time correlation functions from the observed spectra is to compute them. This is particularly attractive because it is the earlier time dynamics which determine the more gross features of the spectrum. The considerable interest in time-dependent methods as reflected in these proceedings is no doubt related to this inherent advantage. Our own interest is however in the dynamics as such with special relevance to unbound systems. The possibility of mode selective chemistry,[52] as mentioned in the introduction, is an important motivation. Here, we review two recent studies, one in the gas phase[53] and one in solution,[54] which were based on the use of classical dynamics: An ensemble of initial conditions which represents the initially prepared non-stationary state, is generated. Trajectories are then propagated and the time correlation function is computed.

Four molecules at energies both below and above their dissociation threshold were studied in the gas phase[53]: CH_3ONO, C_2H_4, SiF_4 and the large (by our standards) trinitro *s*-triazine (RDX). Initial excitations included both mode selective and random deposition of the energy. The computations were run for 10 ps, which is short for thermal unimolecular reactions where the excess energy is low. We have however examined all four molecules also at an energy where their lifetimes for dissociation are comparable or shorter than 10 ps.

The central conclusion of this work, parts of which are still in progress, is that on the timescale of 10 ps mode mixing is very incomplete. This is reflected both in the behavior of the time correlation functions and in the resulting spectra. Figure 4 is a typical outcome for SiF_4 at an excess energy of 75.8 kcal/mole. The time autocorrelation of the SiF stretch modes even at longer times is still distinct from that of the FSiF bends. Many more results are available in the full report.[53]

For all molecules there is a very clear initial drop of $|C(t)|^2$. As expected from the earlier discussion of the Slater model, this drop is most extreme for the many mode RDX molecule. However, this drop (quite moderate for SiF_4, figure 4), does not represent any loss of selectivity of the initial excitation. Taking figure 4a as an example, the initial drop of $|C(t)|$ means that a single SiF stretch is not a good zero order mode. Rather, it should be better thought of as a linear superposition of the stretch normal modes. These rapidly dephase with respect to one another, but the energy remains in the stretches. Plucking an SiF stretch shows no spectral activity in the bend region. The same incomplete energy scrambling is seen even well above the dissociation threshold, figure 5. (Note that the energy of SiF_4 is high enough for dissociation to take place in less than 10 ps.).

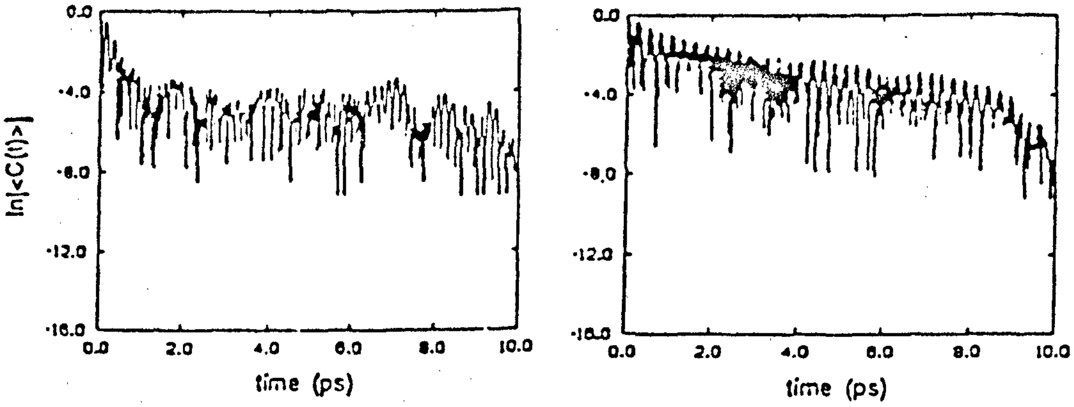

Figure 4. Ln $|C(t)|$ vs. time (in ps) for SiF_4 excited to the $v = 4$ level of all normal modes (excess energy of 75.8 kcalmol^{-1}). Left panel: For the SiF stretch mode. Right panel: for the FSiF bend mode. (Adapted from ref. 53).

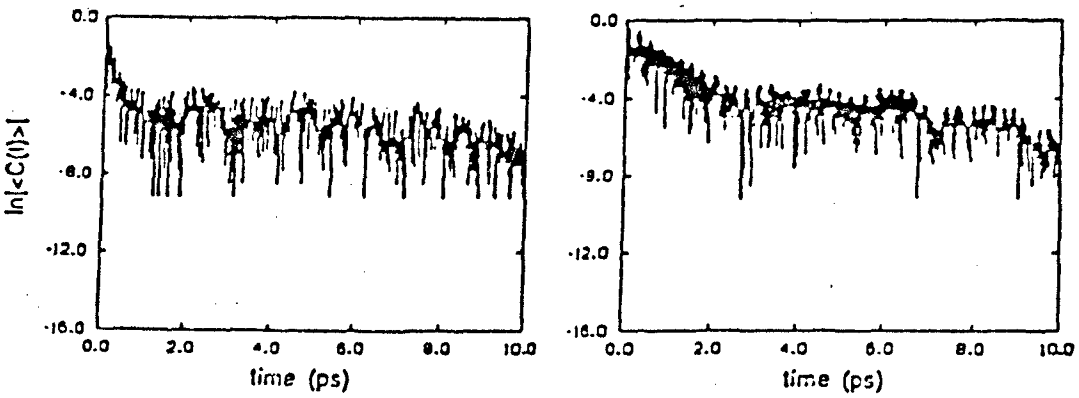

Figure 5. Same as figure 4 but for SiF_4 excited to well above the dissociation threshold. The lifetime is shorter than 10 ps yet the density in phase space is not uniform for times well over 2 ps. (Adapted from ref. 53).

The onset of mode mixing occurs later and precludes the full recurrence of $|C(t)|$. It is important to note that in these polyatomics, the recurrence time can be quite long. A simple estimate is as follows. Say the initially prepared state is a stretched bond. Recurrence means that this bond is again stretched to the same extent. The mean time between two such events is just what is computed in the Slater theory: In that model, the dissociation lifetime of a molecule equated to this mean recurrence time.

SiF_4 is a prototype of molecules which have been excited by infrared multiphoton absorption. Such experiments have typically tended to support extensive energy scrambling in the pumped molecule.[1,55] Our work suggests that this conclusion may well reflect the long duration of the typical CO_2 lasers used in these experiments. (At least in the ns scale if not longer). It should therefore be of interest to return to such experiments but with pulse lengths in the ps range.

The computations in the liquid[54] studied the time evolution of HOCl pumped to the $v = 6$ overtone of OH. This provides sufficient energy to dissociate the weak OCl bond. Yet there are good reasons to expect the very non-resonant energy flow from the OH to the OCl stretch to be quite hindered[56] and to proceed primarily via the bend. The novel feature, very evident in the simulations,[54] is the significant enhancement of this intramolecular energy transfer by collisions with the surrounding Ar liquid. This was particularly evident when the spectrum $S(\omega)$ is computed not over the entire time history (as it should be) but over a narrower time window. This results, of course, in a broad spectrum, devoid of fine structure. However, the three vibrational modes of HOCl are so different in their frequency that for a time window of, say, 1 ps, one can readily discern the three (two stretches and the bend) spectral regions. Such studies clearly demonstrate that the intramolecular vibrational energy redistribution is slow enough that the collisions with the atoms of the liquid can exercise a beneficial effect. From an overall kinetic point of view, the density of the liquid has additional roles.[54] It can cage the dissociation products. It can also remove energy by collisions with the activated HOCl molecule. Even so, at low densities, the primary role of the surrounding Ar atoms is to enhance the intramolecular energy transfer.

CONCLUDING REMARKS

As can be seen from the results presented here, the selectivity of the initial excitation may well persist on time scales comparable to the lifetime of an unbound molecule. This means that the system has not enough time to sample all the energetically accessible phase space before dissociation occurs.

In highly excited polyatomic molecules, the recurrence time $t_r = \hbar\rho(E)$ ($\rho(E)$ is the density of states), for which the sampling of phase space is by definition completed, is very long. From the standard expression[57] of the RRKM rate constant $k(E)$

$$k(E) = \frac{N^*(E - E_0)}{\hbar\rho(E)} ,$$

($N^*(E - E_0)$ is the number of states of the transition state and E_0 the threshold energy), one can see that the fraction of molecules $\exp(-N^*(E - E_0))$ that have not dissociated by t_r is very small since $N^*(E - E_0)$ is typically very large. It is therefore not complete sampling of phase space which needs to be assumed for the validity of statistical theories of unimolecular reactions. In other words, the probing of phase space by the dissociation process is a coarse grained one.

We have recently argued[30] that more than the completeness of the sampling of phase space, it is its representativity which matters to insure the validity of statistical theories. It is well known[46,58,59] that the individual rate constants of the quasibound states in an energy interval $(E, E + dE)$ fluctuate around an average value $k(E)$ which can be estimated by the RRKM theory. Therefore, by representative sampling, we mean that the average rate calculated from the fraction of the quasibound space which has been sampled agrees with the value obtained from RRKM theory. In the case where the localized initial excitation sequentially explores regions of phase space coupled to different product channels, selectivity might be expected.[60]

We have studied[30] the competition between the two processes: mode mixing and dissociation. Here, the two relevant observables are the autocorrelation function $|C(t)|^2$ which probes the persistence of the memory of the initial excitation and the survival probability of the bound subspace B,

$$P(t) = Tr[B\rho(t)] \quad .$$

The entropy $S_B(t)$ of the ME density matrix normalized in bound space $B\rho(t)/P(t)$ is the measure of the volume sampled.

Particular attention has been devoted to the amount of mixing of the initial state and to the role of overlapping resonances. The fact that resonances overlap can be easily understood from the RRKM equation of the rate constant: the ratio of the width $\hbar k$ and the mean spacing $1/\rho(E)$ is large, ($\hbar\rho(E)k = N^*(E - E_0) \gg 1$). This means that the rate matrix[61] Γ is off-diagonal or, in classical terms, that there are recrossings at the barrier. Or, in a more pictorial language, there is a healing[62] of the broken bond. Under such circumstances, the RRKM rate constant is only an upper bound and the system might have enough time to sample phase space before dissociating. Our numerical results[30] show that due to recrossings the rate of exploration of phase space is indeed increased but not enough to lead to a representative sampling before the dissociative process occurs.

Incomplete mixing and sequential exploration of phase space depend in a very sensitive fashion on the sharpness of the localization on the initial state. We find that even a small amount of spreading in the initial state (less than 10% of the available phase space is initially accessed) is sufficient to provide a substantial sampling of phase space before dissociation and thus to insure the validity of statistical theories.

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Appendix C:

INTRAMOLECULAR DYNAMICS

This appendix, by F. Remacle and R.D. Levine, is the latest review of our work on intramolecular dynamics.

It was presented at a NATO meeting in March 1992 and is published as a chapter in 'Time Dependent Quantum Molecular Dynamics: Experiment and Theory'.

x

INTRAMOLECULAR DYNAMICS

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INTRODUCTION

The temporal evolution of an initially prepared nonstationary state of a polyatomic molecule is discussed. Particular attention is given to the short time evolution which can be probed by spectroscopic experiments. It is suggested that the time evolution is often sequential, with separation of time (or, equivalently, of frequency scales). The relevance to mode selective chemistry (in both the gas phase and in solution) is emphasized. In particular it is argued that the very shortest time scale identified from the spectrum is typically shorter than the time scale for mode mixing which is of interest in statistical theories of unimolecular dissociation.

BACKGROUND

On the one extreme are direct bimolecular reactions[1]. A well studied prototype is the abstraction of an H atom by Fluorine[2-4] $RH + F \rightarrow R + HF$. Even for a large polyatomic, molecule RH, much of the reaction exoergicity is carried away as internal excitation of HF. The mechanical picture is quite clear: The newly formed hot HF bond is coupled to R for one or, at most, a few of its (very rapid) vibrations. There is not enough time for the energy in the 'hot spot' to be dissipated over all the available degrees of freedom of RHF. Our question is 'how rapidly does such a hot spot delocalize' and, even more important for us, 'is the dissipation a simple process or does it have fairly well defined stages'. That there is an opposite extreme where, given enough time, the initial hot spot is very delocalized is clearly borne out by the chemical activation experiments[5-10] especially, those of

Resonance Raman scattering cross sections, as a function of the excitation frequency, are being reported for excited states of polyatomic molecules both in the gas phase[1-4] and in solution.[5,6] The time-dependent interpretation[7-9] of Raman spectroscopy provides a link between the measured frequency dependent cross section and the dynamics on the excited potential energy surface(s). Specifically, the resonance Raman scattering amplitude is given in the Condon approximation as the (half) Fourier transform of a time dependent amplitude $< f | \exp(-iHt/\hbar) | i >$ between the initial non stationary state on the upper surface and the final state. This enables one to develop both physical models and semiquantitative short time approximations for the interpretation of the main features of the Raman excitation profile.[1,8-15] As discussed in detail in ref. 3 a more precise agreement between the computed time crosscorrelation function and the observed excitation profile requires a detailed knowledge of the relevant excited potential energy surface(s).

The theoretical route up to now has been from the potential energy surface(s) via a computed time crosscorrelation function to the spectrum. The half (positive times only) Fourier transform relation from the time dependent amplitude to the scattering amplitude precludes the direct inversion of the Raman cross section to yield the time correlation function. This, in contrast to absorption spectroscopy, where the time dependent amplitude can be directly determined as an inverse Fourier transform of the frequency-dependent absorption cross section.[7,8,16-19]

The ability to determine the time autocorrelation function directly from the observed absorption cross section has opened the way towards a better understanding of short time intramolecular dynamics.[16-23] Even when the potential is accurately known so that the time autocorrelation function can be computed (e.g. ref. 19), its more physically intuitive meaning suggests that it, rather than the cross section, provides the better meeting ground between experiment and theory.

The time autocorrelation function, as determined from the absorption cross section gives the probability to remain in the initially accessed non stationary state. It provides however no insight as to where the initial state has propagated to. The latter is determined by the time crosscorrelation function. The inversion of excitation frequency dependent Raman scattering cross sections to time crosscorrelation function is thus of general interest and is the topic of this Letter. An approach which is also capable of yielding the scattering amplitude but which is quite different in details is the 'transform theory'[24] which seeks to determine the Raman excitation profile from the absorption cross section.

The Raman cross section for scattering from state i to state f is proportional to the absolute square of the scattering amplitude

$$\alpha_{fi}(\omega) = (i/\hbar) \int_0^\infty \exp(i\omega t) C_{fi}(t) dt \quad . \tag{1}$$

Here ω is the laser frequency, $C_{fi}(t)$ is the time dependent amplitude, $< f | \exp(-iHt/\hbar) | i >$, we are after and, for the time scale of interest to us here, we did not include in (1) the radiative damping of the excited state. There are two technical difficulties in inverting (1). The first is that the experiment only determines $|\alpha_{fi}|^2$, whereas for inverting (1) one needs the real and imaginary parts separately. The half Fourier transform in (1) suggests that $\alpha_{fi}(\omega)$ be regarded as the full Fourier transform of the 'causal' function $U(t)C_{fi}(t)$ where $U(t)$ is the unit step function. Most texts which discuss the Fourier transform of causal functions explicitly or implicitly make the assumption that they are real and proceed to establish a Hilbert transform relation between the real and imaginary parts of their Fourier transform, here $\alpha_{fi}(\omega)$. However, our $C_{fi}(t)$ is not necessarily real so that all that one can establish in general is[25] that the even and odd parts of $\alpha_{fi}(\omega)$ are related as Hilbert transforms. We therefore proceed as in the derivation of dispersion relations in other branches of scattering theory[26] and assume that, as a function of $s = i\omega$, $\alpha_{fi}(s)$ is analytic and has no zeroes in the right half of the complex s plane, Re $s>0$.[27] This implies that $\ln(\alpha_{fi}(s))$ is analytic for Re $s>0$ which is the condition we need for a unique inversion. One can also use this condition to establish dispersion relations between the real and imaginary parts of $\ln(\alpha_{fi}(s))$. Since $\mathrm{Re}\ln(\alpha_{fi}) = \ln(|\alpha_{fi}|)$ is known from experiment these dispersion relations can in principle be used to determine the phase of α_{fi} (which is the imaginary part of $\ln(\alpha_{fi})$). We have implemented such a procedure and will report on it in detail in the full account of this work. Here we just say that this route is workable and quantitative but not quite as numerically accurate as the route we now describe.

Specifically, we write

$$|\alpha_{fi}(\omega)|^2 = 1/\sum_{r=-n}^{n} \lambda_r \exp(i\omega t_r) \quad . \tag{2}$$

The $2n+1$ expansion coefficients λ_r satisfy $\lambda_{-r} = \lambda_r^*$ because $|\alpha_{fi}|^2$ is real. The time points t_r are not necessarily all equally spaced. The numerical values of both the λ_r's and the t_r's is determined by a procedure of maximum entropy[28,29] as is discussed below. The assumed analytical properties of $\alpha_{fi}(\omega)$ are needed to show (e.g., A. Papoulis, ref. 27, *loc. cit.*) that (2) leads to a unique form $\alpha_{fi}(\omega)$ which we write as $\alpha_{fi}(\omega) = 1/(\sum_{r=0}^{n}(a_r + ib_r)\exp(i\omega t_r))$ with real a's and b's. The λ_r's are, of course, bilinear in the a_r's and b_r's. The condition $\lambda_r^* = \lambda_{-r}$ insures that the number of unknowns be the same. IF we take all the t_r's to be equally spaced then (2) is equivalent to the, so called, Burg spectrum[30,31] and the a's and b's can then be determined by the Levinson algorithm.[31] This provides an easy route for an initial guess and does result in a realistic $C_{fi}(t)$. However, it leads to a periodic function $|\alpha_{fi}(\omega)|^2$, which is not physical, and a superior representation of $\alpha_{fi}(\omega)$ is obtained when the t_r's are not all equally spaced.

From the experimental spectrum one can determine $R_{fi}(t)$, the Fourier transform of $|\alpha_{fi}(\omega)|^2$. The functional form (2) is obtained[28] as that of the most probable (for a distribution of maximum entropy) form of $|\alpha_{fi}(\omega)|^2$ subject to given numerical values of $R_{fi}(t)$

at the given set of times t_r. λ_0 is the multiplier which insures that the area under $|\alpha_{fi}(\omega)|^2$ equal $R_{fi}(0)$. The values of the Lagrange multipliers, λ_r, are determined by the algorithm of ref. 32 with two modifications: (1) The entropy is written as $\int d\omega \ln|\alpha_{fi}(\omega)|^2$ with the maximum being sought not directly as a function of the λ_r's but by varying the (equivalent) set of unknown a_r's and b_r's on which $\alpha_{if}(\omega)$ itself depends. (2) Once a given value of the maximum of the entropy is secured, by optimising the a_r's and b_r's for a given set of t_r's, a new set of t_r's is sought such that the new maximal value of the entropy is lower. Elsewhere, we shall describe this min-max aspect of the algorithm in detail. In general, we start with equally spaced t_r's and and with trial values for the a_r's and b_r's determined using the Levinson algorithm.[31] The time dependent amplitude $C_{fi}(t)$ is obtained as a Fourier transform of $\alpha_{fi}(\omega)$. Special care is needed to obtain the overall phase of $\alpha_{fi}(\omega)$, which depends on its asymptotic behavior.[33] Even when this care is exercised, a use of a library fast Fourier transform algorithm will often spoil it. A quick but risky route is to take advantage of $C_{fi}(t)$ being guaranteed causal and shift the zero of time to where $C_{fi}(t)$ starts to differ from zero.

Figure 1 compares three time crosscorrelation functions $|C_{fi}(t)|^2$ computed for iodobenzene using equations (3)-(6) of ref. 4 with those obtained by the present inversion from $|\alpha_{fi}(\omega)|^2$. The three results shown correspond to a final state with 1,2 and 3 vibrational quanta in the ν_{11} mode of the B electronic state. Note how the method keeps track of the systematic changes in the time crosscorrelation function for different final states. Nine time values ($n = 9$ in equation (2)) were used to obtain the results. We do not show a comparison of the correct excitation profile and equation (2) because, with $n = 9$ and the min-max algorithm, the fit is quite tight.

General properties of the Fourier transform determine the requirements on the experimental data for a successful inversion. In particular, one needs a spectral range broad enough to generate the entire envelope of the time crosscorrelation function. Also, a good reproduction of the very short time dynamics requires an accurate representation of the asymptotic (high and low ω) shape of $\alpha_{fi}(\omega)$. This is noticeable in the bottom panel of the figure for the 0 → 1 scattering cross section where the asymptotic $1/\omega$ dependence of α_{fi} is not well reproduced since we intentionally truncate our input $|\alpha_{fi}|^2$ to mimic realistic data. On the other hand, note the good reproduction of the relative heights and positions of the main features.

Our considerations can also be used for the absorption cross section. Equation (2) determines both the position and the intensities of all transitions. It is thus of considerable interest in connection with the distribution of spectral spacings and intensities. Elsewhere we shall show how the present developments can be viewed as a direct generalization of the maximum entropy approach[34] to these issues.

It has been shown possible to invert frequency-dependent Raman scattering cross sections so as to determine time crosscorrelation functions. A new maximum entropy algorithm provides an essentially quantitative inversion and an accurate fit of the cross section itself. Only the bare essentials of the approach have been described here and a full account is in preparation for publication. Other aspects not discussed in detail include the implications for the analysis of the exploration of phase space and the representation of spectral fluctuations.

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Figure legend

The directly computed time crosscorrelation functions $|C_{fi}(t)|^2$ (left column) and the results of the inversion using $|\alpha_{fi}(\omega)|^2$, (right column) vs. time (in fs). Other details in the text.