INTRAMOLECULAR DYNAMICS, SPECTROSCOPY AND UNIMOLECULAR REACTIONS

Lecture Notes: Cursos de Verano, Universidad Complutense, Aguadulce, Spain

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I. Unimolecular Reactions

This lecture is divided into two parts. The first part concerns recent developments in the application of RRKM theory to unimolecular reactions. These particular applications are to reactions having large internal motions in the transition state (TS), in particular, hindered but nearly free internal rotations in the TS, e.g., for the reactions[1]

$$NCNO \rightarrow NC + NO \tag{1}$$

$$CH_2CO \rightarrow CH_2 + CO \ . \tag{2}$$

In each case these reactions were photoinduced using nearly monochromatic light. In separate experiments the energy-dependence of the rate constants and the rotational-vibrational quantum state distribution of the reaction products were measured.

The position of the transition state along the reaction coordinate in reactions such as (1) and (2) is energy and angular momentum dependent and can be obtained variationally[1,2] (see below). In RRKM theory the rate constant k_{EJ} of a unimolecular reaction of a molecule having an energy E and a total angular momentum quantum number J is given by

$$k_{EJ} = N_{EJ}/h\rho_{EJ} \tag{3}$$

where N_{EJ} is the number of quantum states in the transition state at the given E and J, ρ_{EJ} is the number of quantum states of the dissociating molecule per unit energy at that E and J, and h is Planck's constant. The transition state occurs at a position

along the reaction coordinate where N_{EJ} has a minimum. One can show that the statistical mechanical "bottleneck" to the reaction occurs at that minimum.

Choosing the best reaction coordinate poses an interesting problem. Klippenstein has generalized the method of finding the reaction coordinate.[3] E.g., in reaction (1) is it the C--N distance between the NC and the NO, or is it the center–to–center distance between the NC and the NO, or some combination of them? The coordinate which gives the smallest N_{EJ} is the best choice, and Klippenstein described a way for finding that choice.

In the transition state of reactions such as (1) and (2) there is a coupling between the internal rotational and the orbital angular momenta for the two newly forming fragments. Such effects are included in the calculation of N_{EJ} :[1,2] The contribution of these coordinates (the "transitional degrees of freedom") to N_{EJ} was calculated using a classical Monte Carlo phase space counting of the quantum states of these low frequency motions. The contribution of the remaining (higher frequency) coordinates to N_{EJ} was obtained by a quantum counting.[1,2] All possible distributions of the energy E between these two classes of modes were included. An approximate potential energy surface was used to make these counts.

In the lecture I also discussed the rotational-vibrational quantum state distribution of the reaction products.[1,4] While RRKM theory was initially designed to calculate only the rate constant of a unimolecular process, it was extended recently[4] to the calculation of the quantum state distribution of the reaction products, by introducing an assumption regarding the dynamical behavior of the fragments after leaving the transition state. The vibrations were treated "vibrationally adiabatically" and the hindered rotations nonadiabatically.[1b,4]

In the lecture I also commented on phase space theory (PST), a theory which assumes that the separating fragments in the dissociation rotate freely in the transition state. In phase space theory the orbital angular momentum quantum number l of those outgoing fragments is (by assumption) a good constant of the

motion in the "exit channel", and the position of the transition state is l-dependent: It occurs at the maximum of an effective potential for the outgoing radial motion, the sum of the long range potential energy of interaction of the separating fragments and the l-dependent centrifugal potential. Instead of (3), one uses, in effect,

$$k_{EJ} = \sum_{l} N_{El}/h\rho_{EJ} \qquad (4)$$

where the summation is over all l consistent with the given E and J.

Differences in results obtained using PST and the above variational RRKM theory, and their similarities in the threshold region (low E), were discussed, and comparisons with experiments were given.[1] An example of results for a k_{EJ} for reaction (2), averaged over the relevant J in the low temperature molecular beam experiments, is given in Fig. 1.

II. Intramolecular Dynamics and Spectroscopy

Much of the lecture dealt with intramolecular dynamics and the spectroscopy of high energy molecules. The experiments which were mentioned and which we have investigated with the aid of theory are the following:

Experiments

1. *High resolution* CH *overtone spectroscopy*[5] *of* $(CX_3)_3YC \equiv CH$.

Here, Y is C or Si and X is H or D. A striking experimental fact is that the Si compounds have a much narrower acetylenic CH overtone linewidth than the corresponding C compounds, even though the density of vibrational states ρ in the Si compound is much higher. (The linewidth is often assumed to be proportional to ρ, and so some other explanation is needed for this result and is described in this lecture.)

2. *"Channel Three" Problem in Benzene*[6]

In spectroscopic experiments related to intramolecular dynamics, namely in the fluorescence spectrum of benzene $(S_1 \rightarrow S_0 + h\nu_f)$, the fluorescence yield rather

sharply disappears when the excess vibrational energy in the S_1 state exceeds ca 3300 cm^{-1}. Moreover, high resolution two-photon Doppler-free spectra reveal that not all the spectral lines emitted from this state disappear: at low J the states with K=0 survive, K being the quantum number for the component of the angular momentum along the six-fold symmetry axis, while at high J only the states with J=K survive. Thus, the spectrum actually simplifies when the energy is increased! For most systems the contrary behavior of increasing complexity of the spectrum with increasing vibrational energy occurs instead.

3. CH *Overtone Spectroscopy of Cold Benzene Beams*[7]

Experimental studies of the v_{CH}=3 overtone in cold molecular beams of benzene have shown a much narrower bandwidth than was formerly believed. The previous experiments on gaseous benzene were performed at room temperature and were inhomogeneously broadened. The problem was to now explain the narrowness of the width and the overall shape of the spectral band.

Theory

In each of these cases a principal problem in formulating a theory is the potential relevance of millions of vibrational or rotational-vibrational quantum states to each phenomenon.[8-10] In each case we introduced a zeroth-order set of states and used an elementary "artificial intelligence search" to select the most important states for the phenomenon. High–order perturbation theory was employed in the selection and in #1 and #3 a diagonalization of the selected states was used. An approximate potential energy surface was employed in each case, using available anharmonic constants for benzene in #2 and #3 and the roughly estimated harmonic and anharmonic constants for #1.

In this lecture, I focus on #1, the acetylenic CH overtone spectrum of $(CX_3)_3YC \equiv CH$.[8] Cubic anharmonic coupling terms were initially used in the calculation of the coupling of zeroth order vibrational states. States coupled to the initially selected v_{CH} state (1 or 2) were selected (the new states differed from the

initial state by three vibrational quanta because of the cubic coupling term). They form the first "tier" of selected states. The states which are coupled to these states form the next "tier" , and so on. (States newly selected for a tier were examined to see if they had been previously selected in an earlier tier and, if so, were placed only in the tier in which they were first chosen.) In this way many tiers of states were selected.

A diagram indicating the energies of the selected states for the first six tiers is given in Fig. 2 for v_{CH}=1. It is seen that the Si compound has a much smaller density of relevant states in the initial six tiers than the C compound, even though ultimately the density of states in the later tiers will be much higher for the Si compound. The internal resonances, which facilitate the exchange of vibrational quanta from the initial zeroth-order state, were much more favorable for the C compound, so explaining the higher density of relevant states in the early tiers for that compound.

The spectral linewidth is largely determined by the set of important states in the early tiers. Five or six tiers were needed to obtain enough states for a statistical estimate of the width. The states in the later tiers largely "fill in the broadened line envelope": The short-time behavior for decay of a state and, hence, the nature of the early tiers, determines the linewidth. The long-time behavior, and so the later tiers, determine the detailed internal structure of the broadened line. (One can see this point by invoking the uncertainly principle.)

The method we employed can be used to predict the widths of experimental homogeneously broadened lines in other molecules, provided approximate anharmonic coupling terms can be estimated and provided that some estimate of the energies of the zeroth-order (harmonic) states can be made. The presence of "dead end states" and the removal of their effect by inclusion of reasonable higher order anharmonicities were described in ref. 8b. (Several dead-end states are seen in the third tier in Fig. 2.) The remaining two studies, #2 and #3, mentioned above also

led to interesting interpretations of the observed experimental data, and the students are referred to the cited articles for details.[9,10]

Acknowledgments: The research on which this lecture was based was supported by the National Science Foundation (U.S.). The research on unimolecular reactions was performed by (now Professor) David Wardlaw and (now Professor) Stephen Klippenstein, that on intramolecular dynamics by Dr. Alexei Stuchebrukhov and Aseem Mehta (#1), by Dr. Adam Helman (#2), and by Dr. Yong-Feng Zhang (#3). My first work on intramolecular dynamics was performed in collaboration with, mainly, (now Professor) Vicente López and with (now Dr.) Steve Lederman.[11] I am particularly indebted to each of these coworkers for the insights which they have provided.

In a separate brief talk at the summer school I also described some personal experiences in research which led to the 1992 Nobel Prize in Chemistry for my theoretical work on electron transfer reactions. The relevant history is described in Ref. 12.

Figures

Figure 1. Plot of rate constant log k_{EJ} for reaction (2) *vs* energy. The PST, RRKM and EXPT. values are indicated (from ref. 2b, first article).

Figure 2. First six tiers of sequentially coupled zeroth-order states in (a) $(CH_3)_3CC \equiv CH$ and (b) $(CH_3)_3SiC \equiv CH$. The first state on the left is the acetylenic CH vibration, $v_{CH} = 1$ (from ref.6a).

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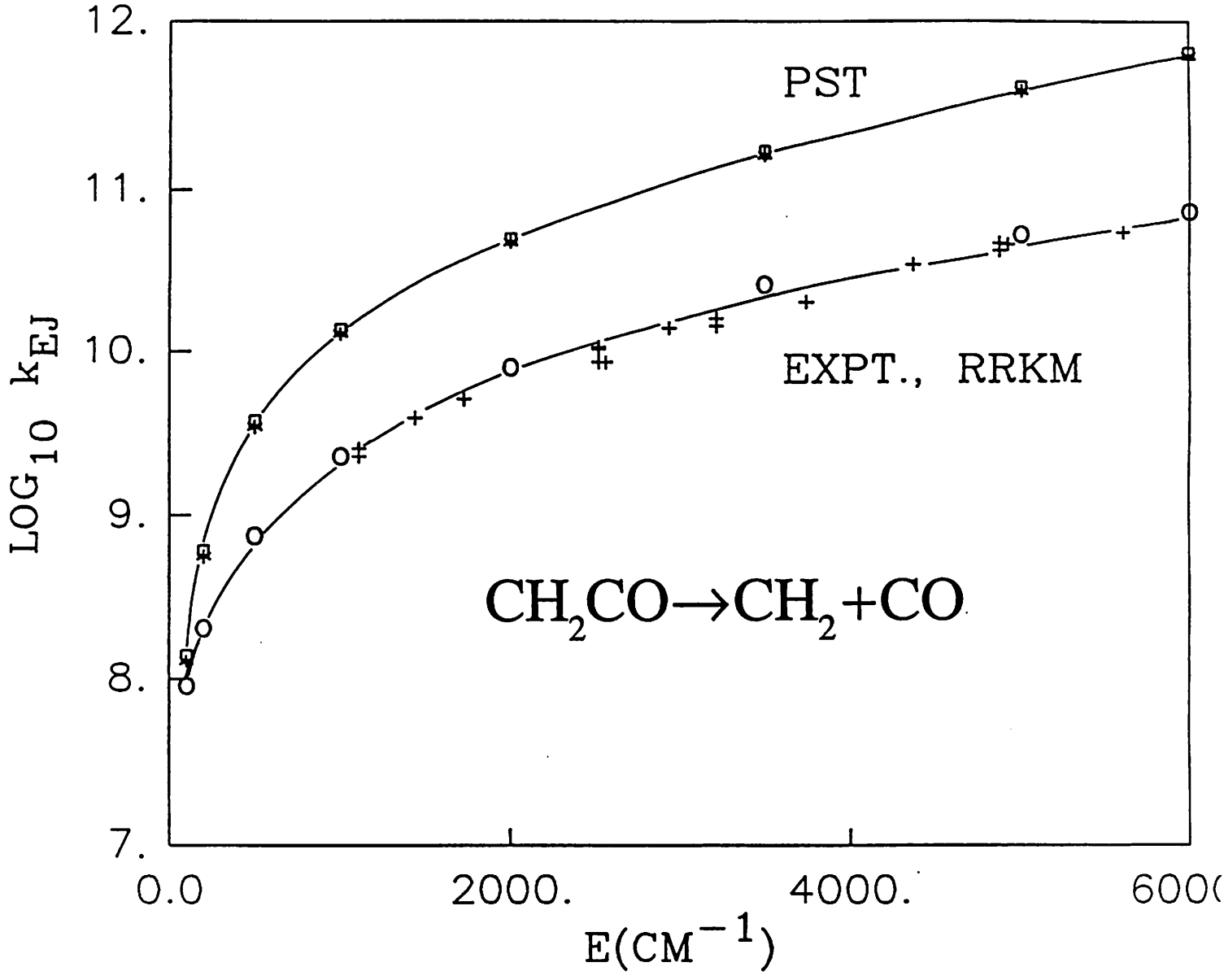
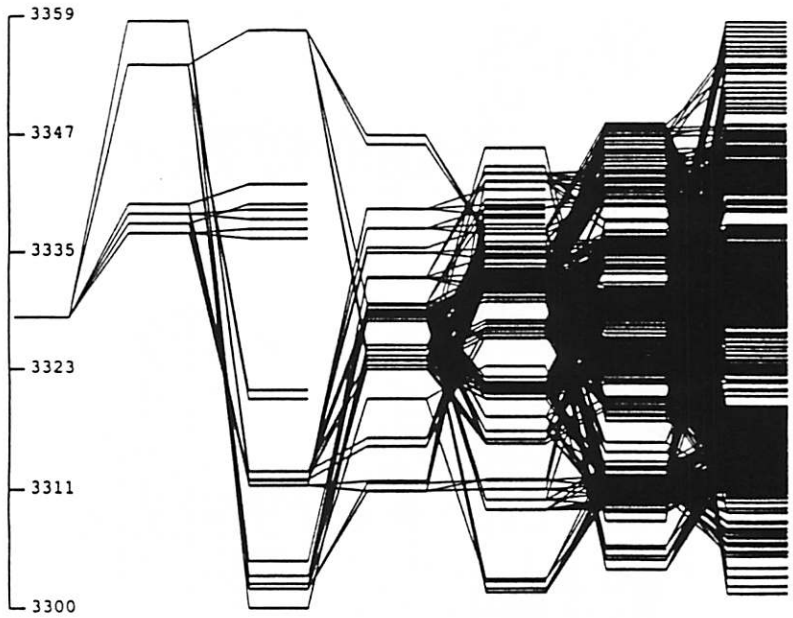

12.
11.
10.
9.
8.
7.
LOG10 kEJ
PST
EXPT., RRKM
CH2CO→CH2+CO
0.0
2000.
4000.
E(CM−1)

Fig. 1

Bottlenecks in tier space

(a) C



(b) Si

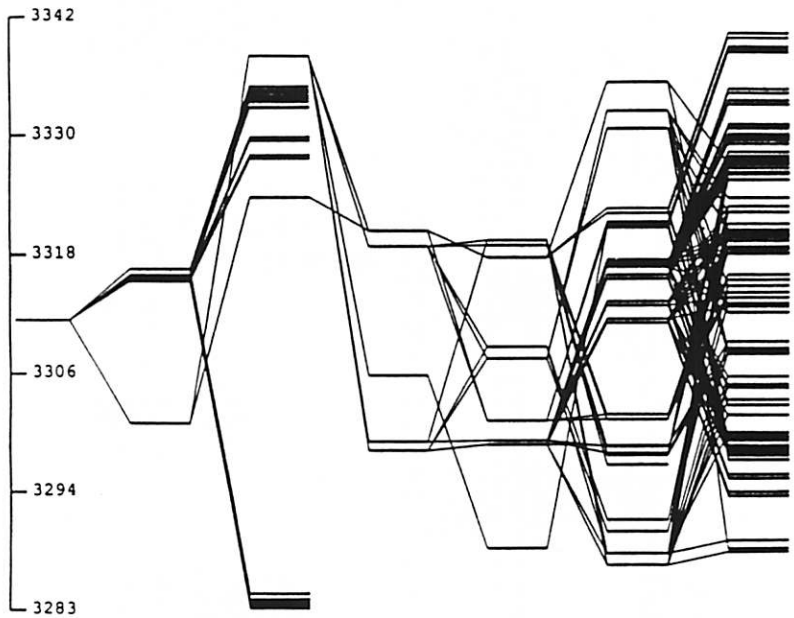


Fig. 2