APPLICATION OF ARTIFICIAL INTELLIGENCE METHODS TO INTRAMOLECULAR DYNAMICS CALCULATIONS

Steven M. LEDERMAN, Stephen J. KLIPPENSTEIN and R.A. MARCUS
Arthur Amos Noyes Laboratory of Chemical Physics [1], *California Institute of Technology, Pasadena, CA 91125, USA*

Received 24 November 1987; in final form 22 February 1988

The application of artificial intelligence (AI) methods to the determination of intramolecular quantum dynamics for multidimensional systems is described. An AI method based on a physically motivated search algorithm and evaluation function is considered. In both the cases of quantum beats and energy "dissipation" the results for the intramolecular vibrational energy redistribution within an eleven-coordinate model system are shown to be accurate with a considerably reduced number of basis states.

1. Introduction

The quantum dynamics of the intramolecular vibrational redistribution (IVR) of energy poses, in general, a quite difficult problem, because of the large number of basis states required for the correct modelling of the physical process. For this reason, many different approaches have been developed for increasing the number of basis states which may be effectively handled in the computations. Sometimes physical arguments have been used to limit consideration to only a few of the degrees of freedom [1]. In other approaches methods such as recursive residue generation [2], partitioning [3], and a generalized moment expansion [4] have been used.

A reduction in the number of basis states to the subset of dynamically important states is an alternative method for solving high-dimensional problems. Recent experimental work has, in fact, provided examples of selective mode coupling among a subset of states [5]. In the present Letter we use an AI method to select the states important to the dynamics and to examine convergence properties. AI methods are particularly well suited to performing the reduction in basis set size and thus more degrees of freedom may be considered, thereby contributing to the study of actual molecular systems.

We describe a method for applying AI to the treatment of the time behavior of an initially prepared vibrational state and apply it to an eleven-coordinate model system. The results from this AI method tend to converge toward the "exact" results as the number of basis states generated by the AI method increases. Examples are given for the cases of quantum beats and of quasidissipative dynamics. AI methods have previously been applied to the study of the dynamics of multiphoton excitation [6] and to the determination of individual eigenvalues [7]. The basis for these applications was the use of AI search methods, as it is here. However, since the present application is to IVR, the search algorithms and evaluation functions presented here are quite different from those given previously.

2. Search algorithm and evaluation function

In the IVR problem the probability distribution function among zeroth-order states is often initially localized and can be represented by a single basis state or a set of basis states. This probability becomes redistributed over some set of final basis states. However, this set of final basis states over which the probability is distributed is not in general known a priori. A search algorithm is discussed next for determining the dynamically important basis states and

[1] Contribution No. 7770.

0 009-2614/88/$ 03.50

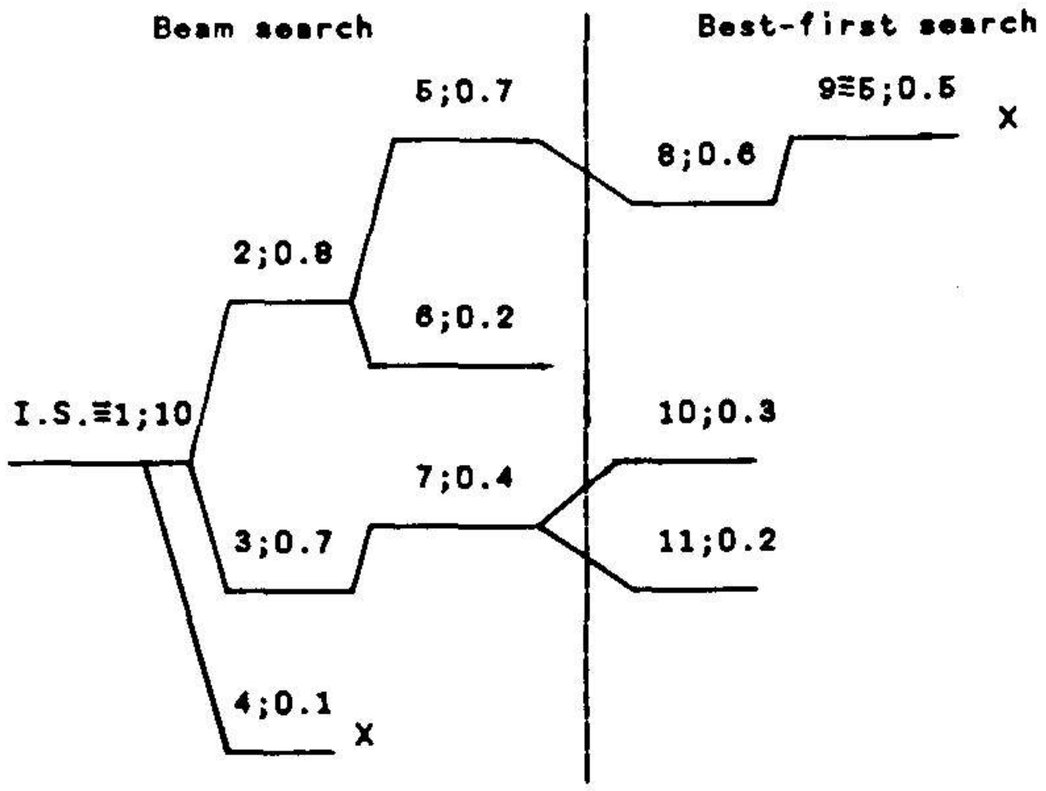

Fig. 1. Example of a best incomplete paths search in which two levels of beam search are performed. The horizontal lines represent states and the dashed diagonal connecting lines represent non-zero couplings. The first number above each line is the number given to the basis state (according to the order in which it is found in the search) and the second number is the evaluation function for the path leading to that basis state.

followed by a description of the evaluation function which is used to estimate the importance of each path in the search process.

The search algorithm, which we have called a *best incomplete paths search*, is a combination of a "beam search" [8] and a "best-fit seach" [8]. A beam search considers all states directly coupled to every incomplete path whose evaluation function is above a certain minimum [#1]. A best-first search considers only the most promising incomplete path as determined by the evaluation function EF for each path (the EF is described later). An example of the search is given in fig. 1, in which the horizontal lines represent basis states with the first number above the line numbering the states in the order searched and the second number giving the evaluation function for the path to that basis state. The first part of the best incompete paths search involves a beam search for the first two levels as seen in fig. 1. In the example, every state directly coupled to the initial state (IS≡1) is found and this yields states 2, 3 and 4. The "X" after state 4 represents the fact that the evaluation function for its path of 0.1 is below the minimum (0.15 say) used for this example, and this path is thus removed from future consideration. The present beam search continues for one more step and all states coupled to states 2 and 3 are found (states 5, 6 and 7). Though the beam search considers many possible choices of paths simultaneously, it necessitates keeping track of a rapidly increasing list of paths. To avoid maintaining an unmanageable list of potential paths, a best-first search is then implemented for all future choices. The beam search is utilized for the first two steps, because poor estimates by the evaluation function at early steps can cause important paths to be discounted unless many possible alternatives are considered.

The best-first search begins at the end of the second level of the two-level beam search. In the example in fig. 1, the path to basis state 5 has the highest evaluation function (0.7) of the three incomplete paths leading to states 5, 6 and 7. All states coupled to state 5 are then found and this yields a path to state 8. There are now three incomplete paths to states 6, 7 and 8, of which the path to state 8 has the highest evaluation function (0.6). When all states coupled to this state 8 are found this only gives state 9, which is a duplicate of state 5. This duplicate state (9) is removed from consideration (marked by "X") since it has a lower evaluation function for its path than the earlier path to state 5 [#2]. Removal of the new path to state 9 leaves two incomplete paths to states 6 and 7 for consideration. Since the evaluation function for the path to state 7 is greatest, all states coupled to state 7 are found to yield the paths to states 10 and 11. The best-first search process of considering the best incomplete path can continue but is stopped here for brevity of presentation.

The states included in the dynamical calculation are the states for those paths with the best evaluation function at each step in the best-first phase of the search. The states along the path are thereby included. In the example in fig. 1, the path up to and including state 5 (states 1, 2 and 5) are chosen first. This is followed by the path to state 8 for which only state 8 has not been previously chosen. Finally, the path to state 7 is included for which states 3 and 7 are new. A new path of states is included for each step in the best-first search. The search process is

[#1] The minimum is chosen through experience to reduce the number of states searched without removing states of importance. A more detailed discussion appears in ref. [9].

[#2] A further discussion of duplicate states and multiple paths to the same state is given in ref. [9].

stopped when a preassigned number of states for the dynamics has been chosen.

The choice of an evaluation function in the present work was based primarily on several considerations: (a) a high weighting for the most dynamically important states must be used in order to encourage these states to be accepted first; (b) the calculation of the evaluation function must be rapid since it has to be determined many times during the searching process; (c) paths should be encouraged to return to an energy near that of the initial state, reflecting the role of the uncertainty principle at long times. The evaluation function given below, motivated by perturbative expressions [10], is a heuristic combination of terms which encourage a return to the initial energy region and which still encourage some searching at energies near that of the previous energy level.

The evaluation function used here in the best incomplete paths seach is given by

$$\mathrm{EF}=\left|V_{12}\prod_{i=2}^{n}\frac{V_{i,i+1}}{\frac{1}{2}(\Delta E_{i,i+1}+\Delta E_{1,i+1})}\right|. \tag{1}$$

Each factor after the product sign was set equal to unity whenever its magnitude exceeds unity (again motivated by perturbation arguments). $V_{i,i+1}$ and $\Delta E_{i,i+1}$ represent the Hamiltonian matrix element and energy difference, respectively, between the i and $i+1$ basis states and $\Delta E_{1,i+1}$ is the energy difference between the initial state and state $i+1$. The evaluation function EF gives an equal weighting to $\Delta E_{i,i+1}$ and $\Delta E_{1,i+1}$ for each state in the path. The evaluation function estimates the importance of the path and is a function of the specific path. The search algorithm compares the magnitude of the evaluation functions for the various states (for the particular paths), and selects states, and their paths, with the largest EFs. It does not maximize (in the sense of setting some derivative equal to zero) the evaluation function for a given state. Other evaluation functions and search methods were studied and are discussed in detail elsewhere [9]. (This more detailed discussion introduces other terms and concepts such as a *goal state* and *expansion* of states.)

After the determination of the important subset of states by the AI procedure the quantum dynamics of the system was then determined by full matrix diagonalization of this subset. From the resulting eigenvalues and eigenvectors the quantities of physical interest were determined.

3. Model system

In the testing of the AI method an eleven-coordinate IVR problem involving a heavy central mass was examined [11]. The model represents the system C_a–C_b–M–CD_2–C_c, where M is a relatively heavy central mass that can act as a barrier to energy redistribution in the molecule, and C and D denote carbon and deuterium atoms [12]. C_a, C_b and C_c have as effective masses those of CH_3, CH_2 and CD_3, respectively. The Hamiltonian for the system is given by the sum of the Hamiltonians for the left and right ligands and the coupling term:

$$H=H_{\mathrm{L}}+H_{\mathrm{R}}+V_{\mathrm{LR}}, \tag{2}$$

where

$$H_{\mathrm{L}}=\tfrac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}P_iG_{ij}P_j + \sum_{i=1}^{2}D_i\{1-\exp[\alpha_i(r_i-r_i^{\mathrm{e}})]\}^2, \tag{3}$$

$$H_{\mathrm{R}}=\tfrac{1}{2}\sum_{i=3}^{12}\sum_{j=3}^{12}\left[P_i\left(G_{ij}+\sum_{k=3}^{12}\frac{\partial G_{ij}}{\partial r_k}r_k\right)P_j\right] + \tfrac{1}{2}\sum_{i=3}^{12}k_i(r_i-r_i^{\mathrm{e}})^2, \tag{4}$$

$$V_{\mathrm{LR}}=\lambda\frac{\cos\theta}{m}P_2P_3. \tag{5}$$

Here, r_i and P_i are the bond coordinate and momentum, respectively. The left Hamiltonian, eq. (3), contains two stretching coordinates and the right Hamiltonian, eq. (4), contains four stretching and five bending coordinates as in a methane-like ligand (but our model system has a reduced C_2 symmetry) [#3]. G_{ij} is the Wilson **G** matrix [13]; **G** and its derivatives in eqs. (3) and (4) are evaluated at the

[#3] The right Hamiltonian, H_{R}, in eq. (4) contains ten bond coordinates, for which one of the bending coordinates is redundant and linearly dependent on the other four bending coordinates. The calculations were performed in symmetry coordinates which remove this redundant coordinate. Details are given in ref. [13].

equilibrium value of the bond coordinates. In eq. (5) θ represents the fixed enclosed angle between the left and right ligand (i.e. the C_b–M–C angle). The detailed parameters used in the model and a detailed discussion of its relevance to IVR calculations are given elsewhere [12].

The approximate separability of the Hamiltonian into the left and right contributions suggested the use of a basis set with its elements given by the product of a wavefunction of a prediagonalized H_L and one of the normal modes of H_R, the latter found when the derivatives of the **G** matrix in H_R are omitted. H_L was prediagonalized because of the high energies of excitation used for the left ligand. The AI technique was applied to vibrational energy transfer between the left and right ligands. The system was initially "prepared" in a basis state that only had excess energy in the left ligand and the amount of energy in the left ligand of the molecule as a function of time was studied.

The λ parameter in V_{LR} permits the variation of the kinetic coupling between left and right ligands in a way which mimicks changing the central mass M. The advantage of using λ instead of actually changing the central mass is that the frequencies of the left and right ligands remain unchanged. Thus, a "pure" mass effect is achieved in this model calculation without the possibility of resonances accidentally being modified.

4. Results

The AI method described in section 2 is compared with the "exact" result, for two different initial states and masses in figs. 2 and 3. These "exact" results involved large calculations that were still practical with presently available computers by imposing a simple energy constraint on the basis states used in the calculation. In order to compare the results of the AI method with these exact results, the AI search was constrained to those basis states used in the exact calculations. These calculations were performed so as to determine the quality of the AI method, with the ultimate goal of using the developed technique without such a constraint on the basis states chosen, both for this and for other systems. In the present comparison, m in eq. (5) is the mass of carbon. In

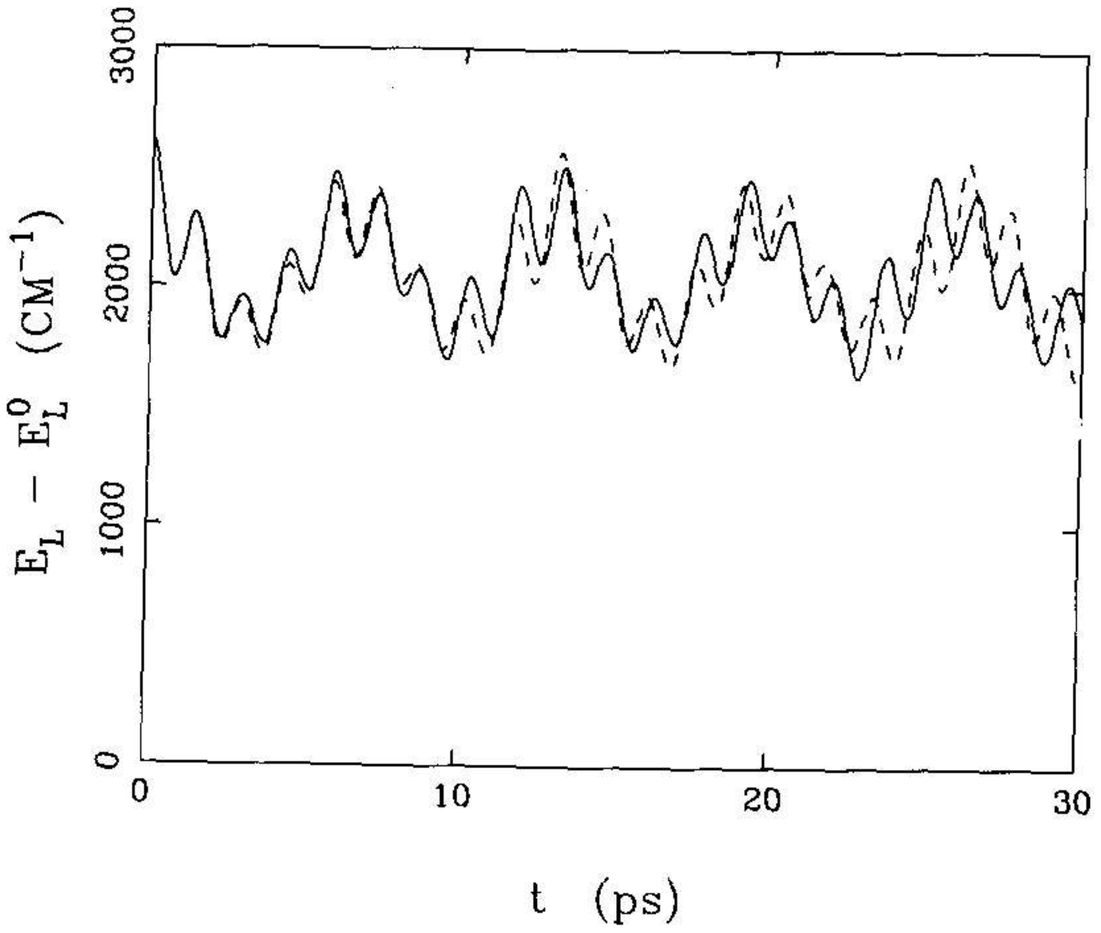

Fig. 2. Comparison of the results for the excess energy in the left ligand plotted versus the time, with $\lambda = 0.1655$ (mass of Ge). The solid line (——) is the exact result, the dashed line (- - -) is the AI result. E_L denotes the energy, and E_L^0 the zero-point energy, in the left ligand.

fig. 2, the basis set for this large, exact calculation consisted of all basis states within an energy of ± 1300 cm^{-1} of the initial state, thereby giving 1023 basis functions. Also, λ was set to 0.1655 to represent the mass of Ge. In fig. 3 twice the mass of carbon was used giving a λ of 0.5, and all basis states within an energy of ± 650 cm^{-1} of the initial state were included, resulting in a basis set size of 1112 for the higher energy excitation.

In the exact calculations, the heavier mass system (fig. 2) displayed vibrational quantum beats, whereas

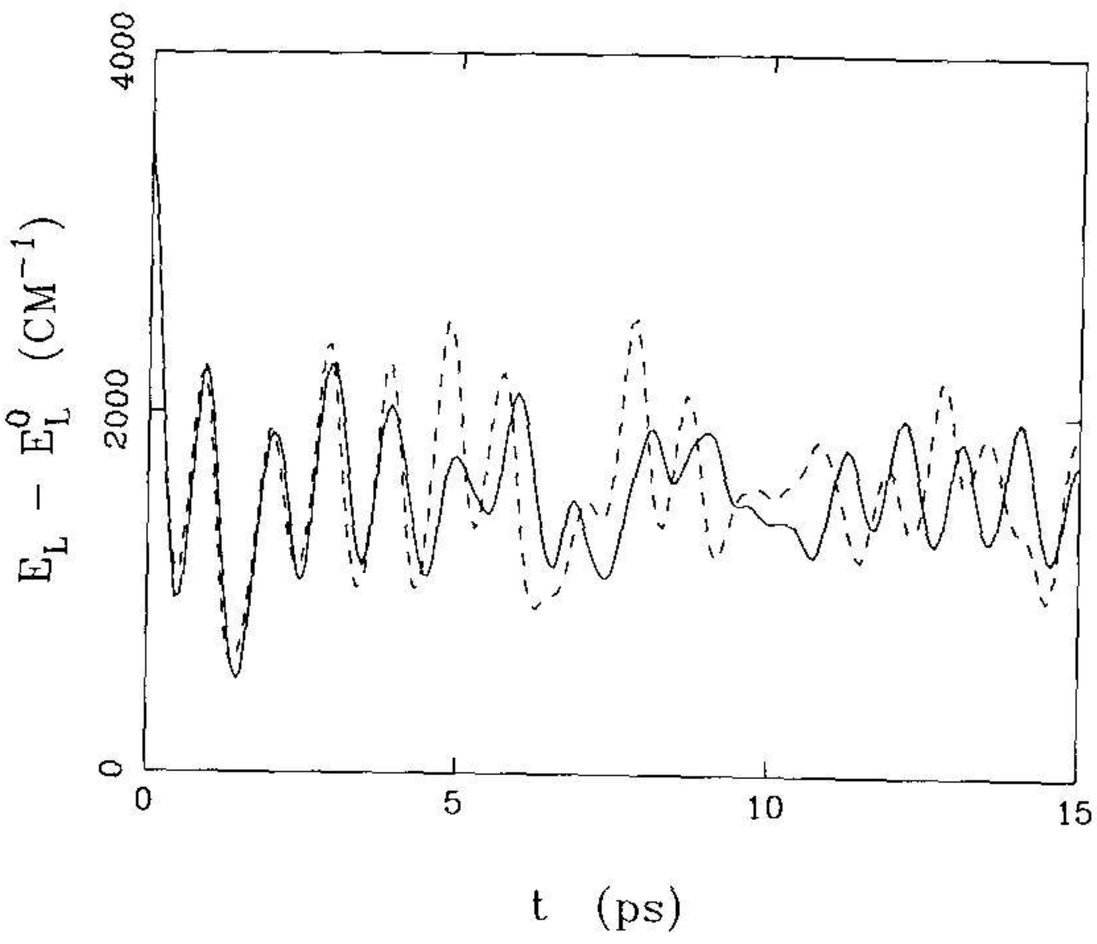

Fig. 3. As in fig. 2 except $\lambda = 0.5$ (twice the mass of C).

the lighter mass system (fig. 3) showed, instead, a greater dissipation of energy from the left ligand into the right ligand. In both cases results from the AI method are seen to be in good agreement with the exact results, especially at short times. Even though the quantum beats case resembles an effective three-state problem, it involved many basis states for an accurate description. Thus, 125 basis states had to be generated by the AI method and used in the calculation of the dynamics in order to obtain good agreement with the exact as given in fig. 2. In a quantum beats case that resembled an effective two-state problem 70 states were needed and will be discussed in ref. [9]. In the dissipative case only 20 states were generated by the AI method for the plot in fig. 3. These two situations, quantum beats and dissipation, represent different dynamical situations and serve to test the robustness of the present AI method.

5. Discussion

The AI method presented here has several attractive features for studying IVR problems with many degrees of freedom. The AI technique can efficiently identify a subset of thousands of dynamically important states from a set of a million or more possible basis states. It should, however, be stressed that the AI search is performed within the set of basis states. Thus, it is still important that an intelligent choice be made for the zeroth-order description of the problem. Without the use of AI searching, the determination of the dynamics within a basis of a million of states is beyond the scope of presently available methods [2–4]. For the examples studied, the time spent in the AI searches is typically only a small fraction of the total computer time (e.g. $<1\%$ for the examples given here) needed to solve the problem. Furthermore, the computer time for the AI search scales linearly with the number of basis states chosen (provided the number of basis states considered scales linearly with the number of basis states chosen, as is the case for the present model problem), but the dynamics scales as a cube of the number of basis states. Thus, the AI search will be a smaller percent of the total computer time for larger problems. Also, the computer time necessary for performing the AI methods on higher energy excitations of a molecule is comparable to that at lower molecular energy excitations, provided that the number of possible states searched by the AI method is the same, even though the total number of available states increase exponentially with energy.

In the present Letter a search algorithm and evaluation function have been presented, and an AI technique has been applied to the determination of the dynamics for two common situations in IVR, quantum beats and dissipation. In the examples given, the AI search method was able to converge towards and represent well the exact calculations. The AI method presented can be readily adapted for use in many problems, since only the description of the Hamiltonian needs to be changed. (A different problem might involve a different choice of search algorithm and/or evaluation function.) Thus, the present AI method is not only promising but can be readily applied to a range of problems.

Acknowledgement

The authors would like to thank Walter Nadler for his help in several aspects of this research, as well as Vicente Lopez and Victor Fairen for their important contributions in developing the model Hamiltonian. It is a pleasure to acknowledge the support of the National Science Foundation, the US–Spain Committee for Scientific and Technological Cooperation, and the Office of Naval Research.

References

[1] K.T. Marshall and J.S. Hutchinson, J. Phys. Chem. 91 (1987) 3219;
J.S. Hutchinson, J. Chem. Phys. 82 (1985) 22;
J.S. Hutchinson, J.T. Hynes and W.P. Reinhardt, Chem. Phys. Letters 108 (1984) 353.
[2] A. Nauts and R.E. Wyatt, Phys. Rev. Letters 51 (1983) 2238.
[3] G.A. Voth and R.A. Marcus, J. Chem. Phys. 84 (1986) 2254;
S.J. Klippenstein, G.A. Voth and R.A. Marcus, J. Chem. Phys. 85 (1986) 5019.
[4] W. Nadler and R.A. Marcus, J. Chem. Phys. 86 (1987) 6982.
[5] W.R. Lambert, P.M. Felker and A.H. Zewail, J. Chem. Phys. 75 (1981) 5958;
P.M. Felker and A.H. Zewail, Phys. Rev. Letters 53 (1984) 501; J. Chem. Phys. 82 (1985) 2961;

U. Schubert, E. Riedle and H.J. Neusser, J. Chem. Phys. 84 (1986) 5326;
E. Riedle, H.J. Neusser and E.W. Schlag, J. Phys. Chem. 86 (1982) 4847.

[6] J.V. Tietz and S.-I Chu, Chem. Phys. Letters 101 (1983) 446;
J. Chang and R.E. Wyatt, Chem. Phys. Letters 121 (1985) 307; J. Chem. Phys. 85 (1986) 1826, 1840.

[7] J. Chang, N. Moiseyev and R.E. Wyatt, J. Chem. Phys. 84 (1986) 4997.

[8] A. Barr and E.A. Feigenbaum, The handbook of artificial intelligence, Vol. 1 (HeurisTech Press, Stanford, 1981) ch. 2;
N.J. Nilsson, Problem-solving methods in artificial intelligence (McGraw-Hill, New York, 1971) chs. 1–5;
P.H. Winston, Artificial intelligence (Addison-Wesley, Reading, 1984) ch. 4.

[9] S.M. Lederman and R.A. Marcus, J. Chem. Phys, to be published.

[10] A. Messiah, Quantum mechanics, Vol. 2 (North-Holland, Amsterdam, 1963) ch. 16, section 16.

[11] V. Lopez, V. Fairen, S.M. Lederman and R.A. Marcus, J. Chem. Phys. 84 (1986) 5494;
S.M. Lederman, V. Lopez, G.A. Voth and R.A. Marcus, Chem. Phys. Letters 124 (1986) 93;
V. Lopez and R.A. Marcus, Chem. Phys. Letters 93 (1982) 232.

[12] S.M. Lederman, V. Lopez, V. Fairen, G.A. Voth and R.A. Marcus, J. Chem. Phys., to be submitted for publication.

[13] E.B. Wilson, J.C. Decius and P.C. Cross, Molecular vibrations (Dover, New York, 1955).