Inversion of Ultrafast Pump-Probe Spectroscopic Data

Roi Baer and Ronnie Kosloff*

Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel

Received: May 26, 1994; In Final Form: August 9, 1994[®]

Spectroscopic observables are governed by the dynamics on the ground and excited potential energy surfaces. An inversion scheme is presented to iteratively construct the potential surface which reproduces experimental data. Special attention is drawn to the nonlinear character of the inversion problem and, in particular, to the role of ultrafast pump-probe spectroscopy for dealing with it. The regions of inversion, i.e., the nuclear configurations for which the potential is to be determined, are identified by calculating the observable-potential sensitivity function. A method is introduced for calculating these sensitivity functions in a numerically converged time-dependent quantum mechanical fashion. These functions are the basic building blocks of the inverted potential. Two demonstrations of the procedure are presented, both use simulated pump-probe spectroscopic data. The first, applied to the ICN molecule, reconstructs the medium- and long-range parts of the dissociative excited surface. The second attempts to reconstruct the bound excited potential surface of NCO.

1. Introduction

In recent years ultrafast pump-probe experiments have matured considerably. From an esoteric discipline criticized for reproducing experimental data already known in the frequency domain, the method is now standing on its own right. Initially, the main asset of time domain methods was insight, derived from the natural tendency to think about molecular encounters in causal terms where a dynamical process is initiated by the pump pulse and followed through time by the probe pulse. Recently experimental ultrafast techniques have been able to compete with frequency domain methods for bound systems in supplying quantitative information on molecular dynamics.¹ For unbound systems with intermediates and in condensed phases ultrafast techniques supersede frequency domain methods. In this paper it is shown that the unique features of time domain spectroscopy can be exploited to give new quantitative results concerning the molecular structure and properties, by enabling inversion of potential energy surfaces.

Molecular processes can be elucidated using the adiabatic theorem, which exploits the fact that nuclear motion is slow compared to the stir of the underlying electrons. The resulting picture is one in which the electron energy eigenvalues form potential energy surfaces, on which the nuclear motion is executed.² Thus, in principle, the molecular energy surfaces can be calculated from first principles just by solving this eigenvalue equation. Ab initio methods for performing this task are today very advanced but still lack, for many systems, the accuracy demanded by quantitative dynamical calculations. The inversion methods attempt to overcome this limitation and design techniques which correct the ab initio predictions using experimental data.

The weakness of the inversion process is that frequently more than one possible potential can faithfully reproduce the laboratory measurements, so that additional assumptions have to be made. In the theory of mathematical inversion these assumptions usually impose analytical properties as well as other known features on the potential surface, e.g., the asymptotic vanishing of the potential and its derivatives for large internuclear distances. Even under such stringent conditions, mathematical inversion procedures are effectively limited to one dimension, because of the large degree of underdetermination in higher dimensions.

Historically, the model problem of the field has been the inversion of central potentials using elastic scattering cross sections and phase shifts.^{3,4} The nonuniqueness of the inversion was lucidly demonstrated by Newton³ as he constructed a nonzero central potential to yield zero phase shifts for all orbital angular momentum l at a given scattering energy. Despite these, Shapiro and Gerber⁵ have shown it possible to use the Born series expansion in order to invert molecular potential energy surfaces from elastic amplitudes. A good summary of scattering data inversion can be found in the book by Newton.⁶

For inversions using rovibrational spectroscopic measurements, the semiclassical Rydberg-Klein-Rees (RKR) scheme is most widely used to determine diatomic potential curves.⁷⁻⁹ The method is based on locating the distance between the inner and outer classical turning points of the potential. As in other inversions, here too nonuniqueness exists, as it stems from the fact that mappings of the potential, which preserve the action between turning point pairs, produce the same observed spectrum.¹⁰ The shortcoming of the RKR method is that it is inherently one dimensional since the multidimensional analogue of "turning points" is undefineable. To overcome this limitation, Gerber and Ratner^{11,12} utilized the self-consistent field (SCF) approximation in order to break down the multidimensional space into a coupled set of one-dimensional systems. These are then inverted by the RKR method sequentially, and an iterative procedure is used to solve the self-consistent set of coupled equations. A different approach to rovibrational spectroscopy inversion is the perturbation based scheme worked out by Kosman and Hinze.^{13,14} This method is based on minimizing the sum of the differences squared between measured term values and calculated energy levels by varying the underlying potential surface using an inverse perturbation approach.

The difficulty in direct inversion has led to the use of heuristic indirect procedures. These are based on hypothesizing a parametrized functional form for the potential and use the empirical data to fit the parameters. This approach can be used

[®] Abstract published in Advance ACS Abstracts, February 1, 1995.

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in conjunction with the known functional form of the potential for diatomic fragments. The main drawback of the heuristic approach is that it is arbitrarily dependent on the functional form of the potential chosen for the modeling; thus good fits are hard to obtain.

Another technique of inversion, especially suited for bound polyatomic systems, is based on the expansion of the potential surface in a Taylor series around its minimum and it systematically alters the coefficients in order to obtain a fit to experimental data.¹⁵ Recently, McCoy et al.¹⁶ improved these methods by exploiting fourth-order Van Vleck perturbation theory.

Direct inversion procedures have been revived lately, especially by Rabitz and co-workers^{17–20} as well as by the present authors.²¹ A comprehensive review of methods and numerous applications for inverting scattering and rovibrational spectroscopic data by Rabitz et al. has recently been published.²² The Rabitz approach consists of iteratively improving upon an initial best-guess potential. The method is based on functional sensitivity analysis and uses the Tikonov regularization method to overcome the inherent instabilities caused by the ill-posedness of the inversion problem.

In this paper the pump-probe ultrashort pulse spectroscopy is used for direct potential surface inversion. The goal is to use explicitly the special characteristics of pump-probe experiments, which have made them so appealing to intuition. The basic motivation for the work²³ has been the classical mechanical inversion procedure of Bernstein and Zewail²⁴ for the ICN photodissociation on the excited-state potential. Although the classical inversion scheme has been criticized by Krause et al.,²⁵ this study shows that a full quantum inversion of pump-probe experiments is possible and that the optimal inversion scheme follows closely the causal classical picture. For this purpose a new direct inversion method is developed, applicable for excitedstate potential surfaces, as well as for the ground-state case.

Following Rabitz and co-workers,²² functional sensitivity analysis is used as the basic tool for inversion, thus linearizing the problem. Solving the linearized equation employing all experimental data simultaneously limited the inversion to cases where the initial guess potential was very close to the final form. It should be stressed that this effect is caused by the highly nonlinear nature of the pump-probe inversion problem. Thus, the main point of this paper is how to cope with the nonlinearity of the inversion. It is found that by starting from areas in which a good knowledge of the potential exists, one can gradually build into the ambiguous regions. This makes explicit use of local aspects of the sensitivity functions. It was found that the pump-probe experiments have extreme sensitivity to the Franck-Condon region of the potential, therefore this section should be determined from other experiments. For this reason the inversion scheme from absorption spectra of photodissociating molecules was developed.²¹ The pump-probe inversion enables us to go beyond the Franck-Condon area, and the desired region of inversion, the sensitivity region, can be controlled by the experimentalist.

The scope of the inversion can be extended beyond the simple Zewail type pump-probe experiments. The procedure can employ phase-locked ultrashort pulses similar to the type used by Scherer et al.²⁶ but using strong field pulses, of which the pump is a complex pulse, specially designed to create high vibrational excitation on the excited potential surface. As a demonstration for inverting this type of spectroscopic data, we present a two-dimensional inversion of the bound excited-state potential of NCO.

The arbitrariness of the procedure is minimized, by using all available information on the form of the target potential surface, ab initio data and intuition included. All this is incorporated during the construction of an initial guess, called the reference potential. The iterative procedure developed in the following sections than alters this potential surface until the experimental measurements are reconstructed. The first step is to map out the regions of the potential to which the measurements are sensitive, using high-quality quantum mechanical methods for simulating the experiment. After the sensitivity functions are obtained, their structure is scrutinized and the appropriate form of inversion is decided upon.

The simulation of the experiment and the calculation of sensitivity functions is performed using the combination of the Fourier grid representation of the wave function with the Chebychev polynomial expansion of the evolution operator. These mehods have been shown to provide extremely accurate and stable results.^{21,27-30} The method was used to calculate directly the absorption²⁹ or Raman spectra²⁷ of weak field excitation. In a previous paper, we used these methods to efficiently invert frequency domain absorption spectra into the excited potential of ICN molecule at the Franck–Condon region.²¹ The paper demonstrates that by exploiting the special features of time domain spectroscopy, inversion of the medium-and long-range parts of the potential energy surface can also be performed.

The section structure of this paper is as follows. In section 2 the theory and the calculation algorithms for performing the fully quantum mechanical inversion is presented. This section is divided into four subsections. Section 2A presents the inversion theory, together with the basic algorithm proposed for solving it. The basic concept of this scheme is the sensitivity function, about which theory and calculation methods are presented in subsection 2B, for Hamiltonian dynamics and in subsection 2C for the Liouvillian dynamics. A new algorithm for performing the time integral of two wave functions, needed for the calculation of sensitivity functions but useful for other applications in molecular dynamics, is given in subsection 2D. The inversion theory is applied to two case studies, where simulated experimetnal data were used to reconstruct the underlying potential surface. The first case study, presented in section 3 is that of the Zewail ultrashort pump-probe experiment for inverting an excited-state surface of the ICN molecule. The second case study, shown in section 4, reconstructs bound excited-state potential of NCO, using phase-locked strong field pulses.

2. Inversion Scheme

A. Inversion Equation. The inversion problem is intimately related to the postulates of quantum mechanics since it addresses the central issue of measurement. Considering the measurement of an observable A, quantum mechanics differentiates between the state of the system and the operator \hat{A} that corresponds to the observable. Only a combination of the two entities yields the observed measurement result A. This statement is summarized by Von Neumann in the following equation:³¹

$$A(t) = \operatorname{tr}\{\hat{\varrho}_{t}\hat{\mathbf{A}}\}$$
(2.1)

where the state of the system is represented by the density operator $\hat{\varrho}_t$. When this state is a pure state, it may then be described by the wave function $\Psi(t)$, leading to the formulation

$$A(t) = \langle \hat{\mathbf{A}} \rangle = \langle \Psi(t) | \hat{\mathbf{A}} | \Psi(t) \rangle$$
(2.2)

Equations 2.1 and 2.2 represent the static postulate of quantum mechanics. The objective of the inversion procedure is to deduce the exact forces governing the nuclear motion from the observed values of various time dependent experimentally measurable entities. For a nondissipative system this motion

is generated by the Hamiltonian

$$\hat{\mathbf{H}}(t) = \hat{\mathbf{T}} + \hat{\mathbf{V}} + \hat{\mathbf{W}}(t)$$
(2.3)

where $\hat{\mathbf{T}}$ is the nuclear kinetic energy operator, $\hat{\mathbf{V}}$ is the potential energy operator, and $\hat{\mathbf{W}}(t)$ is a known time-dependent perturbation, caused by an external, experimentally controllable, source. Since both the kinetic energy and the external perturbations are known, the target for inversion is the potential energy operator, composed of the Born-Oppenheimer potential energy surfaces, and possibly some nonadiabatic coupling terms.

For the present theoretical analysis it is more convenient to use the Heisenberg picture, where it is the operator which is time dependent, while the state of the system is fixed. In this picture the motion of the operator A in time is determined by the following similarity transformation:

$$\hat{\mathbf{A}}(t) = \hat{\mathbf{U}}^{\dagger}(t,0) \,\hat{\mathbf{A}}\hat{\mathbf{U}}(t,0) \tag{2.4}$$

where the evolution operator $\hat{\mathbf{U}}(t,0)$ is a unitary transformation governed by the Schrödinger equation and boundary condition:

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$$i\hbar \,\mathrm{d}\hat{\mathbf{U}}/\mathrm{d}t = \hat{\mathbf{H}}(t)\,\hat{\mathbf{U}}(t,0); \qquad \hat{\mathbf{U}}(0,0) = \hat{\mathbf{I}}$$
(2.5)

The theoretical prediction of the experimentally observed value of \hat{A} at time t, as given by eq 2.2, is thus determined by the operator $\hat{\mathbf{V}}$. To conclude, the time dependence of the observable $A(t) = \langle \hat{\mathbf{A}}(t) \rangle$ is a functional of the potential $\hat{\mathbf{V}}$. This functional is nonlinear and in general has a very complicated form.

The Schrödinger equation is a recipe for predicting experimental measurements, once the potential is given. Is it possible to invert this procedure? Can the potential operator be determined from experimental data? It is the purpose of this paper to give a partially positive answer to these questions. Furthermore, a detailed method for carrying out this inversion procedure is now described.

Assume that M experimentally measured results a_m (m = 0, ..., M - 1) are obtained by M different experimental setups, corresponding respectively to M observables \hat{A}_m . The theoretical prediction for the measured values, the quantum mechanical expectation values A_m , are M functionals of the potential and the inversion problem is now a problem of solving the following M functional equations:

$$A_m(\hat{\mathbf{V}}) = a_m \quad (m = 0, ..., M - 1)$$
 (2.6)

Since these equations are nonlinear, they are solved iteratively, starting from an initial best estimate potential, called the reference potential $\hat{\mathbf{V}}_{ref}$, that yields, when inserted into the functional A_m , values which deviate by δa_m from those observed:

$$A_m(\hat{\mathbf{V}}_{ref}) = a_m - \delta a_m \quad (m = 0, ..., M - 1) \quad (2.7)$$

If the reference potential is close to the true potential $\hat{\mathbf{V}}$, the difference $\delta \hat{\mathbf{V}} = \hat{\mathbf{V}} - \hat{\mathbf{V}}_{ref}$ is everywhere small, then a linear equation relating $\delta \hat{\mathbf{V}}$ to δa_m is obtained:

$$J_m \delta \hat{\mathbf{V}} = \delta a_m \qquad (m = 0, ..., M - 1) \tag{2.8}$$

where J_m is the sensitivity functional of the *m*th observable to the potential: it operates on the $\delta \hat{\mathbf{V}}$ operators to give a number. Symbolically

$$J_m = \mathrm{d}A_m/\mathrm{d}\hat{\mathbf{V}} \tag{2.9}$$

Equation 2.8, in the limit of $\delta \hat{\mathbf{V}} \rightarrow 0$ is in fact the definition of the operator derivative in eq 2.9.

The linearized inversion eq 2.8 must now be solved. The successful linearization of the inversion does not remove the ill-posedness of the problem. Bertero³² gives an excellent review of linear inversion problems and methods of their solution. In this study the equations were solved by expanding $\delta \hat{\mathbf{V}}$ as a linear combination of M operators $\hat{\mathbf{B}}_m$:

$$\delta \hat{\mathbf{V}} = \sum_{m} b_m \hat{\mathbf{B}}_m \tag{2.10}$$

where the $\hat{\mathbf{B}}$ operators are called targeting operators since they will be used to localize the sensitivity functional, and b_m are expansion coefficients, solutions of the following $M \times M$ linear equation:

$$\sum_{m'} (J_m \hat{\mathbf{B}}_{m'}) b_{m'} = \delta a_m \tag{2.11}$$

Here, the highly nonunique nature of the inversion problem is evident: for different choices of the $\hat{\mathbf{B}}$ operator, different solutions are obtained. It should be stressed that although the ill-posedness is removed by choosing a certain $\hat{\mathbf{B}}$ operator, the resulting equations can still be ill-conditioned. This issue will be addressed in the case-study sections.

For the present inversion schemes the potential is diagonal in the R representation therefore the sensitivity functional, when applied to a function f(R), acts to multiply it by the sensitivity function $J_m(R) = dA_m/dV(R)$ and integrate the result over R:

$$\hat{J}_m f = \int J_m(R) f(R) dR = \int (dA_m/dV(R)) f(R) dR$$
 (2.12)

Just as for the potential, the $\hat{\mathbf{B}}$ operator is assumed diagonal in *R* representation:

$$\hat{\mathbf{B}}_m \to B_m(R) \tag{2.13}$$

To calculate these entities, a realization by discretizing the R space on a mesh of N grid points R_n with spacing ΔR_n is constructed. Thus transforming the potential difference to a Nvector $\delta V_n = \delta V(R_n)$, and the sensitivity functional J to a $M \times$ N matrix with $J_{mn} = J_m(R_n)\Delta R_n$. In matrix notation eq 2.8 then becomes

$$J\delta V = \delta a \tag{2.14}$$

This is the discretized inversion equation. Typically, the number of equations M is much smaller than N, the totality of unknown δV_n 's, because these represent a continuous R space, while the former are a finite count of measurements made. Since there are more unknowns than equations, the linear system (2.14)admits at least N - M independent solutions. As immediately verifiable by insertion into eq 2.14, a general solution is obtained by the following expression:

$$\delta V = B^T (JB^T)^{-1} \delta a \qquad (2.15)$$

where B^T is an $N \times M$ matrix, constructed so that the square M $\times M$ matrix, JB^{T} is nonsingular. This equation is the discretized analogue of eq 2.11, and the columns of the B^T matrix are actually the $B_m(R)$ of eq 2.13.

Since δV is not determined uniquely by eq 2.15, there is room left to permit the incorporation of a priori knowledge concerning the inverted potential. This can be achieved by a suitable choice of the $B_m(R)$ targetting functions which linearly combine to form δV .

It is important to consider the nonlinear nature of the inversion problem (see eq 2.6). Since the equations are solved by linearization, the reference potential must be very close to the "true potential". It is found that good results are obtained typically for deviations of 0.01 eV. But this limitation can be relaxed and deviations of even more than 0.1 eV can be dealt with if the special features of pump-probe observables are

exploited. The pertient feature of the pump-probe observable is the fact that its sensitivity function is usually well localized in the nuclear configuration space. Furthermore, by altering the pump and probe pulse parameters, it is possible for the experimentalist to control and determine the domain of high sensitivity. Therefore, by choosing different pump-probe parameters, the experimentalist can "see" different sections of the potential surface.

Since the sought-for potential is usually known to high accuracy in certain regions (e.g., pump Franck–Condon and asymptotic regions), the inversion process can start from one of these and gradually enter the locations in which it is vague. Thus the first iterations are based on the experimental setups that are sensitive to sections close to the "known part" of the potential. After inverting the potential in this region, additional experimental results are added, extending a bit further into the "unknown parts". Thus, each iteration alters the potential surface in a new section, adjacent and overlapping the region modified in the previous one, paving the way for its successor. This way, the specific section of the potential surface being currently under construction is always close to the "true potential". An algorithm for implementing this idea is outlined forthwith:

(1) Select a sequence of experimental setups (observables) that gradually build sensitivity from nuclear configurations in which the potential surface is accurately known into areas in which it is inexact. One way to do this, which works well in the cases studied, is to use "probe-resonance pulses". Practically, this means that for each time delay in an ascending series of times t_m (m = 0, ..., M - 1) the probe wavelength λ_m which yields maximum probe absorption (or induced emission, depending on the experiment) is located, the series $a(\lambda_m, t_m)$ thus obtained, is used as the sequence of observables for the inversion process.

(2) Set M = 1. Set V—the target-of-inversion potential to the above-mentioned best-estimate potential surface, which is highly accurate at asymptotic regions and at the pump Franck—Condon region.

(3) Set $V_{ref} \leftarrow V$.

(4) Calculate the V_{ref} based expectation values a_m^{calc} and compare with the results measured in the laboratory to determine $\delta a_m = a_m^{\text{calc}} - a_m^{\text{empi}}$.

(5) Calculate the sensitivity functions $J_m(R_n)$ on the grid representing the potential.

(6) Calculate the required potential correction δV using eq 2.15. The B^T columns should be built out of the sensitivity functions themselves, so that δV obtained is zero at nuclear configurations for which the observable sensitivity functions are zero. The most natural choice is to take $B_m(R_n) = J_m(R_n)$. This however is not always a good choice, since the sensitivity function $J_m(R)$ can have undesirable features, such as highfrequency oscillations, that should not be built into the potential. It was found that these high-frequency oscillations once formed in the potential tend to be amplified in successive iterations yielding unphysical potential energy surfaces and damaging the stability of the inversion process. One way to overcome this is to choose smooth B^T columns, which nevertheless resemble the sensitivity function's essential structure (smooth peaks for instance). This point is application dependent and is discussed in the specific case studies in sections 3 and 4.

(7) Correct the potential surface: $V \leftarrow V_{ref} + \delta V$.

(8) Add an experiment from the sequence prepared in step (1): $M \leftarrow M + 1$. And redo from step 3, unless the experiment sequence is exhausted.

To apply the algorithm, two crucial quantities have to be calculated. The first is the expectation value $A(t) = \langle \hat{A}(t) \rangle$ (step

4), and the second is the sensitivity function $J(R) = dA/d\hat{\mathbf{V}}(\mathbf{R})$ (step 5). Equations 2.1 and 2.2 give working expressions for expectation values; the method of calculating the sensitivity functions will be described in the following subsections. The resulting expressions, as shown in section 2B are readily available from efficient numerical calculations.

B. Sensitivity Function under Hamiltonian Dynamics. The time-dependent operator $\hat{A}(t)$ depends on the potential \hat{V} through the evolution equation (2.4). An infinitesimal change $\delta \hat{V}$ in the potential will, in the Heisenberg picture, cause a corresponding variation in the operator $\hat{A}(t)$. This induced change is given by

$$\delta \hat{\mathbf{A}}(t) = \hat{\mathbf{U}}^{\dagger}(t,0) \, \hat{\mathbf{A}} \delta \hat{\mathbf{U}}(t,0) + \text{hc} \qquad (2.16)$$

The change in $\hat{\mathbf{U}}$ can be expressed, using first-order time-dependent perturbation theory, as

$$i\hbar\delta\hat{\mathbf{U}}(t,0) = \int_0^t \hat{\mathbf{U}}(t,\tau) \,\delta\hat{\mathbf{V}}\hat{\mathbf{U}}(\tau,0) \,\mathrm{d}\tau$$
 (2.17)

Plugging this result into eq 2.16, yields the causality relation between the cause $\delta \hat{\mathbf{V}}$ and the induced change in the observable $\delta \hat{\mathbf{A}}(t)$:

$$i\hbar\delta\hat{\mathbf{A}}(t) = [\hat{\mathbf{A}}(t), \int_0^t \delta\hat{\mathbf{V}}(\tau) \,\mathrm{d}\tau]$$
 (2.18)

where $\delta \hat{\mathbf{V}}(\tau)$ is defined by

$$\delta \hat{\mathbf{V}}(\tau) = \hat{\mathbf{U}}^{\dagger}(\tau, 0) \,\delta \hat{\mathbf{V}} \hat{\mathbf{U}}(\tau, 0) \tag{2.19}$$

We now assume that nonadiabatic couplings are kept constant, and therefore $\delta \hat{\mathbf{V}}$ is a diagonal operator in the $|R\rangle$ representation, and

$$\delta \hat{\mathbf{V}} = \int \mathrm{d}R \; |R\rangle \delta V(R) \langle R| \tag{2.20}$$

(Note that the integration can also include summations on discrete indexes: R can represent both continuous variables and discrete quantum numbers.) We can now return to the wave-packet Schrödinger picture, and the expectation values, at the measurement time t, of the two equated entities in eq 2.18 are easily cast into the following form:

$$\delta A(t) = (2/\hbar) \int \mathrm{d}R \ \delta V(R) \ \mathrm{Im}(\int_0^t \mathrm{d}\tau \ \chi^*(R,\tau) \ \Psi(R,\tau)) \quad (2.21)$$

where

$$\Psi(\tau, R) = \langle R | \hat{\mathbf{U}}(\tau, 0) | \Psi_0 \rangle \qquad (2.22)$$

is the coordinate representation of the state of the system, $|\Psi_0\rangle$ is the initial state, and

$$\chi(\tau, R) = \langle R | \hat{\mathbf{U}}^{\dagger}(t, \tau) \hat{\mathbf{A}} | \Psi(t) \rangle \qquad (2.23)$$

Note that χ is a wave packet carrying the measurement information: it depends on the form of the operator which represents the observable. Now, the sensitivity function of $A(t) = \langle \hat{A}(t) \rangle$ with respect to the changes $\delta V(R)$ is deduced from eq 2.21 and the operator derivative definition eq 2.9 becomes in the *R* representation, a functional derivative:

$$\delta A(t)/\delta V(R) = (2/\hbar) \operatorname{Im}(\int_0^t d\tau \, \chi^*(R,\tau) \, \Psi(R,\tau)) \qquad (2.24)$$

Notice that the product $\chi^*(R,\tau) \Psi(R,t) = \langle \chi(\tau)|R \rangle \langle R|\Psi(\tau) \rangle$ is the probability amplitude for a transition from state $|\Psi(\tau)\rangle$ to state $|\chi(\tau)\rangle$ at the point R. The state $\chi(\tau)$, characterized by the final condition $\chi(t) = \hat{A}\Psi(t)$, is evolved backward in time. Consequently, the sensitivity function becomes proportional to the imaginary part of the sum over all times of the transition amplitudes at the position R between the forward moving wave function $\Psi(\tau)$ and the backward moving information carrying wave function $\chi(\tau)$.

It is interesting to examine the expression for the sensitivity function (eq 2.24) in a simple case for which the induced variation in the expectation value is immediately apparent. Adding a constant to the potential should not change the dynamics and therefore the expectation values. Consider a constant change in the potential $\Delta V_i(R) = \text{constant}$. Using the definite form for the previously arbitrary basis $|R\rangle$, it is composed of continuous R's (e.g., nuclear configurations) and discrete j's (e.g., quantum numbers of electronic eigenstates). The change in the observable $\langle A(t) \rangle$ is computed by multiplying the sensitivity function by this constant and then integrating over all R and summing over all j. To be consistent, this process must yield zero change in $\langle A(t) \rangle$. Consequently, the total integral of the sensitivity function must be zero, which should of course be the case for the above form of the sensitivity function. This can indeed be proved as follows. First, note the fact that the $|R,j\rangle$ basis is complete and therefore

$$\sum_{j} \int \mathrm{d}R \; |R,j\rangle \langle R,j| = \hat{I} \tag{2.25}$$

Next, for any intermediate time τ :

$$\sum_{j} \int dR \, \chi^*(R,\tau) \, \Psi(R,\tau) =$$

$$\sum_{j} \int dR \, \langle \Psi(t) | \hat{\mathbf{A}} \hat{\mathbf{U}}(t,\tau) | R_{,j} \rangle \langle R_{,j} | \hat{\mathbf{U}}(\tau,t) | \Psi(t) \rangle =$$

$$\langle \Psi(t) | \hat{\mathbf{A}} | \Psi(t) \rangle = \langle \hat{\mathbf{A}}(t) \rangle \quad (2.26)$$

This quantity is real because \hat{A} is Hermitian; therefore, the total integral of the sensitivity function, proportional to its imaginary part, must be zero, QED.

C. Sensitivity Function under Liouvillian Dynamics. Real experiments are described by mixed initial states and usually by dissipative evolution. The formalism of the sensitivity function has to be extended to include mixed states and non-Hermitian Liouville operators.

A brief sketch of the formalism to be used here is presented. The inner product between two operators is defined by

$$(\hat{\mathbf{A}} \cdot \hat{\mathbf{B}}) = \operatorname{tr}\{\hat{\mathbf{A}}^{\dagger} \hat{\mathbf{B}}\}$$
(2.27)

The definition of the inner or scalar product is used to construct a Hilbert space of operators also known as the Hilbert–Schmidt space.^{33,34} This means that any operator can be expanded as a linear combination of a complete set of operators.

The linear operators which map the operator space into itself are called superoperators. A definite example is the "Liouvillian" \mathcal{L} , defined by

$$\mathscr{L}_{\mathcal{A}}\hat{\mathbf{A}} = -(i/\hbar)[\hat{\mathbf{V}},\hat{\mathbf{A}}] = -(i/\hbar)(\hat{\mathbf{V}}\hat{\mathbf{A}} - \hat{\mathbf{A}}\hat{\mathbf{V}}) \quad (2.28)$$

The normalized state of the system is represented by a density operator $\hat{\varrho}$ which is a Hermitian unit-traced linear operator,³¹ and the dynamics of the system is governed by the Liouville von Neumann equation:

$$d/dt \,\hat{\varrho}(t) = \mathcal{L}_{H}\hat{\varrho} = -(i/\hbar)[\hat{\mathbf{H}}(\mathbf{t}), \hat{\varrho}(t)] \qquad (2.29)$$

This equation is the starting point for many generalized treatments of quantum systems coupled to heat baths or systems undergoing random external perturbations.³⁴ Dissipative terms \mathcal{L}_{D} added to \mathcal{L}_{H} yield the system's Liouville superoperator \mathcal{L}_{t}) = $\mathcal{L}_{H} + \mathcal{L}_{D}$, and the generalized Liouville equation is then

$$d/dt \,\hat{\varrho}(t) = \mathcal{A}(t) \,\hat{\varrho}(t) \tag{2.30}$$

The time evolution operator which corresponds to the Liouville equation is the superoperator $\mathcal{R}(t,0)$, which contrary to the purestate, isolated system, case is nonunitary. This superoperator evolves in time according to eq 2.30, and the solution for $\varrho(t)$ is formally written as

$$\hat{\varrho}(t) = \hat{\mathscr{G}}(t,0) \ \hat{\varrho}(0) = \hat{\varrho}(0) \ \hat{\mathscr{G}}(t,0)$$
 (2.31)

The expectation value of an operator \hat{A} at time t is defined by

$$A(t) = \langle \hat{\mathbf{A}}(t) \rangle = \operatorname{tr}\{\hat{\varrho}(t)\hat{\mathbf{A}}\} = \operatorname{tr}\{\varrho(0) \,\mathcal{E}^{\dagger}(t,0)\hat{\mathbf{A}}\}$$
(2.32)

(cf. eq 2.1). Equation 2.32 paves the way to the "Heisenberg" picture, where the system state is stationary, while the dynamical operators are time-dependent, evolving according to

$$\hat{\mathbf{A}}(t) = \mathscr{I}(t,0) \ \hat{\mathbf{A}}(0) \tag{2.33}$$

The quantity of interest is the variation of the expectation value of the operator $\hat{A}(t)$ when a small change in the molecular potential operator is made. From eq 2.33 it can be seen that this may be obtained once the change in the evolution operator has been figured out. It is explicitly assumed that the change in the evolution operator due to a perturbation $\delta L(t)$ is

$$\delta \mathscr{R}(t,0) = \int_0^t \mathscr{R}(t,\tau) \,\,\delta \mathscr{R}(\tau) \,\,\mathscr{R}(\tau,0) \,\,\mathrm{d}\tau \qquad (2.34)$$

This equation is analogous to eq 2.17 of the pure-state case. It can be proved that a necessary condition for eq 2.34 is that $\Re(t,0)$ is invertible. Even for dissipative dynamics the super-operator of evolution is invertible for finite propagation time. The treatment here is then as general as the assumption that $\Re(t,0)$ is perturbed according to this equation. Using eqs 2.32, 2.33, and 2.34, the induced change in $A(t) = \langle \hat{A}(t) \rangle$ is given by

$$\delta \hat{A}(t) = \int_0^t \operatorname{tr}\{\hat{\varrho}(0) \,\mathcal{E}(\tau, 0) \,\mathcal{L}_{\delta \nu} \mathcal{E}(t, \tau) \,\hat{\mathbf{A}}\} \,\mathrm{d}\tau \quad (2.35)$$

Taking the trace with respect to the R basis in which $\delta \hat{V}$ is assumed diagonal, one obtains

$$\delta \hat{\mathbf{A}}(t) = \int \mathrm{d}R \int_0^t \langle R | \varrho(\tau) \mathcal{L}_{\delta \nu} \mathcal{G}^{\dagger}(t, \tau) \hat{\mathbf{A}} | R \rangle \, \mathrm{d}\tau \quad (2.36)$$

Defining the operator $\hat{A}(t,\tau)$ as

$$\hat{\mathbf{A}}(t,\tau) = \mathscr{F}(t,\tau)\hat{\mathbf{A}}$$
(2.37)

and using the cyclic permutation symmetry of the trace, the final expression for the sensitivity function becomes

$$\delta \hat{\mathbf{A}}(t) / \delta \hat{V}(R) = (i/\hbar) \int_0^t \langle R | [\hat{\varrho}(\tau), \hat{\mathbf{A}}(t,\tau)] | R \rangle \, \mathrm{d}\tau \quad (2.38)$$

As a relatively simple application of this general equation, consider a system initially in a pure state Ψ_0 governed by a dissipative evolution described by a non-Hermitian Hamiltonian. In this case, the time evolution superoperator takes a special form, and eqs 2.31 and 2.37 are written as

$$\hat{\varrho}(t) = \hat{U}(t,\tau) |\Psi_0\rangle \langle \Psi_0 | \hat{U}^{\dagger}(t,\tau)$$
$$\hat{\mathbf{A}}(t,\tau) = \hat{\mathbf{U}}^{\dagger}(t,\tau) \, \hat{\mathbf{A}} \hat{\mathbf{U}}(t,\tau) \tag{2.39}$$

Remember that since the evolution operator $\hat{U}(t,\tau)$ is no longer unitarian, this is neither a similarity nor a unitary transformation (note, however, that $\hat{A}(t,\tau)$ is Hermitian if \hat{A} is). Equation 2.39 may be used to calculate the commutation relation in eq 2.38. The crucial step in this calculation shows that Inversion of Pump-Probe Spectroscopic Data

$$\langle R|\varrho(\tau)\,\hat{\mathbf{A}}(t,\tau)|R\rangle = \Psi(R,\tau)[\langle R|\hat{\mathbf{U}}^{\dagger}(t,\tau)\hat{\mathbf{A}}|\Psi(t)\rangle]^{*} \quad (2.40)$$

Upon insertion of this expression into eq 2.38, eq 2.24 is recovered. This result generalizes that derived in section 2B for purely Hermitian Hamiltonians. There is an important conceptual difference between the two cases. In the case of a Hermitian Hamiltonian eq 2.23 defines the state $\chi(\tau)$ as the backward evolution (from time t to time τ) of state $\Psi(t)$. Now, however, since the evolution operator $\hat{U}(t,0)$ is no longer unitarian, $\hat{U}^{\dagger}(t,0)$ is not a usual "backward evolution", indeed, it is a very special backward evolution, one in which the damping caused by the non-Hermitian terms in $\hat{H}(t)$ is not reconstructed, therefore leading to the loss of information contained in the experimental result from the final time to the past.

D. Numerical Evaluation of Time-Overlap Integrals. A numerical scheme for calculating the time integration of correlation functions constructed from a product of two distinct wave packets is presented in this section. The integration which appears in the right-hand side of eq 2.24 is an example. This type of integral is extremely useful for other applications as well, especially for flux calculations in scattering and reactive scattering problems. The integration scheme will enable a numerically exact integration, without having to propagate the wave packets using extremely small time steps. It will be shown that the integral can be replaced analytically by an infinite series, which in a numerical calculation are truncated.

The integral of interest is given by the following equation:

$$I(t,R) = \int_0^t \chi^*(\tau,R) \,\Psi(\tau,R) \,\mathrm{d}\tau \qquad (2.41)$$

where both $\Psi(t)$ and $\chi(t)$ are two wave functions evolved by the same time-independent Hamiltonian \hat{H} :

$$\Psi(\tau) = e^{-(i/\hbar)\hat{H}\tau}\Psi(0)$$

$$\gamma(\tau) = e^{-(i/\hbar)\hat{H}\tau}\gamma(0)$$
(2.42)

In a previous paper,²¹ a method for calculating the timecorrelation function of two wave packets was presented. The problem addressed here does not resemble a time-correlation integral but can be represented as one. Instead of looking at $\chi(\tau)$ as the forward evolution of $\chi(0)$, it can be thought of as the backward evolution of $\chi(t)$. In this way the time integral is dressed as a time correlation of two wave packets:

$$I(t,R) = \int_0^t [e^{-(i/\hbar)\hat{\mathbf{H}}(\tau-t)}\chi(t,R)]^* e^{-(i/\hbar)\hat{\mathbf{H}}\tau} \Psi(0,R) \,\mathrm{d}\tau \qquad (2.43)$$

The method described in ref 21 may now be gainfully employed and in the following is briefly outlined. First, the two wave packets are propagated using the truncated Chebychev expansion operator: 28,40

$$\Psi(\tau,R) = e^{-i\hat{\omega}\tau} \sum_{n=0}^{N} a_n(\nu\tau) \phi_n(R)$$
$$\chi(\tau,R) = e^{-i\hat{\omega}(\tau-t)} \sum_{n=0}^{N} a_n(\nu(\tau-t)) \theta_n(R) \qquad (2.44)$$

In the series a_n is proportional to the *n*th Bessel function J_n , more specifically $a_n(x) = (2 - \delta_{n0})J_n(x)$. The symbols $\phi_n(R)$ and $\theta_n(R)$ denote the functions obtained by operating with $T_n(\hat{\mathbf{H}}_N)$ respectively on $\Psi(0)$ and on $\chi(t)$, where $T_n(x)$ are the Chebychev polynomials and $\hat{\mathbf{H}}_N$ is the normalized Hamiltonian. These and other symbols are defined in the following equations:

$$\phi_0 = \Psi(0)$$

$$\phi_1 = -i\hat{\mathbf{H}}_N \phi_0$$

$$\phi_{n+1} = -2i\hat{\mathbf{H}}_N \phi_n + \phi_{n-1}$$

$$\hat{H}_N = (2\hat{H} - \hat{\omega})/\nu$$

$$\nu = (E_{\text{max}} - E_{\text{min}})/2\hbar$$

$$\hat{\omega} = \nu + E_{\text{min}}/\hbar$$
(2.46)

With this expansion, the time integral (2.43) becomes

$$I(t,R) = \mathrm{e}^{-i\hat{\omega}t} \sum_{n,m} [\int_0^t a_m(\nu(\tau-t)) a_n(\nu\tau) \,\mathrm{d}\tau] \theta_m(R)^* \,\phi_n(R)$$
(2.47)

At this point a valuable property of the Bessel functions can be used to replace their correlation integral by an infinite series.³⁵

$$\int_{0}^{x} J_{n}(x-y) J_{m}(y) \, \mathrm{d}y = 2 \sum_{k=0}^{\infty} (-1)^{k} J_{n+m+2k+1}(x) \qquad (2.48)$$

Rearranging terms and using eq 2.48 finally enable the time integral (2.41) to be represented by the following expression:

$$I(t,R) = (2/\nu)e^{i\omega t} \sum_{n,m} (-1)^m (2 - \delta_{n0})(2 - \delta_{m0})A_{m+n}(\nu t) \phi_m^*(R) \phi_n(R)$$
(2.49)

there defining the coefficients $A_{n+m}(t)$:

$$A_{n+m}(vt) = \sum_{k=0}^{\infty} (-1)^k J_{n+m+2k+1}(vt)$$
 (2.50)

For a given value of t, the Bessel series $\{J_n(\nu t)\}_{n>\nu t}^{\infty}$ exhibits exponentially rapid decay to zero as n is increased. Therefore, the sums in eqs 2.49 and 2.50 both display exceedingly stable numerical convergence.

3. Case Study 1: Inversion of ICN Excited-State Potential

Following Bernstein and Zewail,²⁴ the pump-probe experiments on the photodissociation of ICN constitute an appropriate example for inversion of the excited-state potential. The original method has been criticized by Krause et al.²⁵ arguing that because of the quantum nature of the process the classically based inversion is inappropriate. Nevertheless in this section it is shown that using a full quantum description, the Bernstein-Zewail idea is fruitful and can lead to a viable inversion procedure.

The experimental setup of the pump-probe experiments and their interpretation have been described in detail by Rosker et al.³⁶ The experiment consists of exposing an ICN molecule, initially in the ground electronic state, to a sequence of two ultrashort laser pulses (see Figure 1). The first pulse, the pump, is designed to shift a portion of the molecular wave function to an excited state of repulsive nature. The second pulse, the probe, carefully timed relative to the pump, interacts with the evolving excited wave packet and creates an amplitude on a third excited state correlated to an excited CN fragment (denoted CN*). Measuring the intensity of fluorescence originating from the radiative decay, the yield of CN* product is determined as a function of the time delay and wavelength of the two pulses. In carrying out the inversion process, it is assumed that the ground electronic potential is known to a fair accuracy and the second excited state is practically structureless with respect to



Figure 1. The three relevant potential energy surfaces for the ICN pump-probe experiment. The molecule is initially in the vibrational ground state of the $X\Sigma^+$ surface. The pump pulse transfers some amplitude to the excited ${}^3\Pi_{0^+}$ state which starts accelerating toward dissociation in response to the repelling force. At a time delay Δt the probe pulse interacts with the molecule and raises some of the amplitude to the CN*-correlated surface, measured by recording the CN* \rightarrow CN fluorescence. The probe-induced excitation is registered as a function of the time delay Δt and probe wavelength ω . Notice that the excited state possesses a potential well with a minimum at $R \approx 6.3$ eV (indicated by a small arrow).

the I-CN internuclear coordinate. Thus the target of inversion is reduced to the first excited repulsive electronic surface.

The simplest quantum mechanical description of this system is obtained by considering three electronic surfaces and only one dynamical degree of freedom, the R_{I-CN} separation. Other possible electronic states, nonadiabatic couplings, as well as other ICN degrees of freedom (bending, CN vibrations) are neglected. Also, for simplicity, the electronic transition dipole operators are taken *R* independent. These approximations, crude as they are, drastically reduce the complexity of the calculations, while retaining the essential physics of the ICN photodissociation and making it possible to explore the inversion possibilities and performance.

The Hamiltonian of the system is denoted³⁷ by

$$\hat{\mathbf{H}}(t) = \begin{pmatrix} \hat{\mathbf{T}} + \hat{\mathbf{V}}_{g} & \hat{\mathbf{W}}_{ge}(t) & 0\\ \hat{\mathbf{W}}_{eg}(t) & \hat{\mathbf{T}} + \hat{\mathbf{V}}_{e} & \hat{\mathbf{W}}_{ef}(t)\\ 0 & \hat{\mathbf{W}}_{fe}(t) & \hat{\mathbf{T}} + \hat{\mathbf{V}}_{f} \end{pmatrix}$$
(3.1)

where the two pulses are described by the radiative coupling terms:

$$\hat{\mathbf{W}}(t) = \hat{\mathbf{W}}^{\dagger}(t) = -\hat{\mu}^{*}(\epsilon_{1}(t)\cos(\omega_{1}t) + \epsilon_{2}(t)\cos(\omega_{2}t))$$
(3.2)

where $\hat{\mu}$ are the dipole operators and $\epsilon_n(t)$, n = 1, 2, are the electric field envelopes of the two laser pulses, both varying slowly relative to the central frequency ω_n^{-1} time scale. Since the delayed CN* \rightarrow CN fluorescence is proportional to the population on surface f, the corresponding observable is the following projection operator:

$$\hat{\mathbf{P}}_{f} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(3.3)

The target of inversion is the first excited-state potential $\dot{\mathbf{V}}_{e}$. Using the formalism developed in section 2, in the *R* representation, the sensitivity function of the observable (3.3) to this potential becomes

$$\delta \hat{\mathbf{P}} / \delta V(R) = (2/\hbar) \operatorname{Im} \{ \int_0^t \chi_e^*(\tau, R) \Psi_e(\tau, R) \, \mathrm{d}\tau \} \quad (3.4)$$



Figure 2. Two normalized transients measured by the CN* fluorescence for the ICN pump-probe setup. The circled curve corresponds to 6 fs pulses, and the diamond curve to 25 fs ones. This figure clearly shows the effect of leveling off the important details of the potential surface.

where t is a time after the laser pulses die out. The ICN molecule is prepared initially on its ground electronic surface $\Psi(0) = \Psi^{o}_{g}$. The following definitions for $\Psi_{e}(\tau)$ and $\chi_{e}(\tau)$ are used:

$$\Psi_{e}(\tau) = \hat{\mathbf{P}}_{e}\Psi(\tau) = \hat{\mathbf{P}}_{e}\hat{\mathbf{U}}(\tau,0) \Psi(0)$$
(3.5)

$$\chi_{e}(\tau) = \hat{\mathbf{P}}_{e}\chi(\tau) = \hat{\mathbf{P}}_{e}\hat{\mathbf{U}}(\tau,t)\,\hat{\mathbf{P}}_{f}\Psi(t) \qquad (3.6)$$

The three relevant potential surfaces are shown in Figure 1 the ground-state surface is cast into the Morse functional form, designed to fit the known dissociation and vibrational excitation energies of ICN. The excited surface is taken as the ${}^{3}\Pi_{0+}$ diabatic surface calculated by Yabushita et al.³⁸ This surface exhibits a potential well at $R_{\rm I-CN} \approx 6.3$ bohr. The second excited surface is independent of R. The two other electronic surfaces, ${}^{1}\Pi_{1}$ and ${}^{3}\Pi_{1}$, are ignored as are the nonadiabatic couplings between ${}^{1}\Pi_{1}$ and ${}^{3}\Pi_{0+}$.

In the original experiments 100 fs (fwhm) pulses were used. These broad pulses have been found to eliminate important details of the potential surface. For example as can be seen in Figure 2, the broad pulse response is not influenced by the potential well of the ${}^{3}\Pi_{0+}$ surface while the shorter pulse is. These considerations naturally lead to the use short pulses of 250 au (≈ 6 fs) for the inversion demonstration. Examples of various transients for these pulses are shown in Figure 3.

To use the inversion algorithm of section 2A, special attention must be paid to the sensitivity functions structure and behavior, since they determine the correct choice of the columns of the targeting matrix B^{T} .

The most striking feature of the sensitivity functions is the dominance of sensitivity in the Franck–Condon region of the pump pulse ($R_{I-CN} \approx 5.2$ bohr), as shown in Figure 4. This dominance means that, unattended, any inversion procedure will make changes almost entirely in this region. To overcome this problem, it is assumed that the potential in this region is known from other sources and therefore is excluded from the inversion target. This region can be determined by an inversion procedure based on the absorption spectra.²¹ Consequently the B^T columns are chosen to ignore the sensitivity at the Franck–Condon region.

An important feature of the sensitivity functions is demonstrated in Figure 5. Here the probe pulse catches most of the excited wave-packet amplitude as it is located on the right wall of the excited potential well. However, since there is still some wave-packet amplitude on the opposite side, it also becomes a sensitivity-determining region, thus yielding a nonlocal sensitiv-



Figure 3. Pump-probe observables for the ICN system: the transient CN* fluorescence intensity is depicted as a function of time delay for various probe wavelengths. The basic probe wavelength is tuned to resonance transition in the asymptotic I-CN separations (diamond curve). The other two curves are offset from this frequency by -0.0653 eV triangles and +0.19 eV circles. The pump wavelength is constant throughout. The pulses' width is 250 au (≈ 6 fs).



Figure 4. Typical sensitivity function, for time delay $\Delta t = 3200$ au (≈ 80 fs). Notice the dominance of the pump pulse's Franck-Condon region ($R \approx 5.2$ bohr), and the far-field sensitivity ($R \approx 10$ bohr).

ity function. This quantum effect of nonlocality, occurring typically inside potential wells, was found to be damaging for the inversion process. Hence, it is imperative to choose the B^{T} columns in such a way as to mitigate the effect of nonlocality.

Another interesting phenomenon in the sensitivity functions is demonstrated in Figure 6 which shows two sensitivity functions corresponding to probe pulses of the same time delay and almost the same frequency, the photon energy difference being 0.007 eV. In fact, the CN* fluorescence intensity following the two pulses is almost identical. Yet, as is seen in the figure, their sensitivity functions are remarkably different. The top curve shows relatively much higher sensitivity and has a constant sign (negative), while the bottom curve has low sensitivity and features a change of a sign. The low-sensitivity curve corresponds to a "resonance pulse" while the high sensitivity one is "off-resonance" (by 0.007 eV). Therefore, as the inversion makes the reference potential surface fit more closely with the true surface, the observable lose sensitivity. Since the inversion method is based on nonsingularity of the matrix JB^{T} (see eq 2.15), losing too much sensitivity can become troublesome and requires special treatment.

To overcome these problems the *m*th column of the targeting B^T matrix has been chosen as a Gaussian $e^{-(R-R_0)^2/2\sigma^2}$. The parameters R_0 and σ depend on the *m*th sensitivity function $J_m(R)$



Figure 5. Sensitivity function corresponding to a time delay in which the excited wave packet is probed while residing mainly on the right wall of the potential well at $R \approx 7.5$ bohr ($\Delta t_{delay} = 1600$ au ≈ 40 fs). This sensitivity function has a double peak since some amplitude still exists on the opposite side of the potential well. The Gaussian *B* targeting function corresponding to this sensitivity function is also shown (dashed).



Figure 6. Two sensitivity functions, with the same time delay (80 fs) but with slightly different frequencies ($\Delta \omega = 0.007 \text{ eV}$). The much higher sensitivity of the Franck-Condon region ($R_{\text{I-CN}} \approx 5.2$ bohr) is not shown.

in the following way:

$$R_0 = \langle R \rangle = \frac{\int (J_m(R))^2 R \, \mathrm{d}R}{\int (J_m(R))^2 \, \mathrm{d}R} \tag{3.7}$$

$$\sigma = 2\sqrt{\langle R^2 \rangle - \langle R \rangle^2} \tag{3.8}$$

The integrations in eq 3.7 are performed on the whole R range excluding the Franck-Condon region. Also, to prevent high-frequency oscillations, σ is constrained to be at least 0.2 bohr. It was found that this choice eliminates the damaging effect of the nonlocality of the sensitivity function and prevents the buildup of high-frequency oscillations. Such a Gaussian function superimposed on the corresponding sensitivity function is shown in Figure 5.

The use of the targetting functions enabled to remove the ill-posedness of the problem, but the resulting equations can still be ill-conditioned. Specific methods have to be devised for dealing with the vanishing of sensitivity functions or, more generally, with a nearly singular JB^T matrix. The standard approach of the singular value decomposition (SVD)³⁹ was chosen. This method locates the (generalized) eigenvalues of any matrix and uses them as indicators of the singular condition of the matrix (the singular condition is defined as the ratio of



Figure 7. ICN inversion progress. Left panel: The dotted line is the true potential, the dashed line is the reference potential and the solid line is the inverted potential, shown in various stages of the inversion. The potential differences are shown on the right panel. The true to reference (a Gaussian) is depicted by a dotted line; the true to inverted difference is traced out by the solid line. The inversion stages are (a) after 15 experiments; (b) after 25 experiments; (c) after 30 experiments; (d) after 50 experiments.

the largest eigenvalue to the smallest one). When a matrix is singular or rank deficient, this ratio is infinite, since at least one eigenvalue is zero. On testing for the optimal maximum condition number which yields a good inversion, a value of 10^4 was found. The SVD ensures that the condition number does not exceed a given value by changing the matrix in such a way that effectively eliminates troublesome sensitivity functions. The maximum condition number should be determined by the magnitude of the experimental error. It should be noted that other methods for dealing with the ill-conditioned equations can also be employed, especially the use of Tikonov regularizations,³² which systematically approximates the ill-conditioned equations by well-conditioned ones.

Figure 7 demonstrates how the inverted potential is gradually reconstructed. The reference potential, identical with the "true" potential near the Franck-Condon region, deviates from it by 0.1 eV in larger distances, over a wide internuclear region of approximately 3 bohr. The transients calculated using the reference potential are significantly different from the "empirical" ones (those calculated using the true potential), as is seen in Figure 8.

The calculation was performed using the Chebychev expansion of the time-independent evolution operator.⁴⁰ Since the pulse induced evolution is time dependent, use was made of the rotating wave approximation eliminating high frequency oscillations enabling, to substantially decrease the number of time steps needed for the propagation. Various parameters concerning the calculations are given in Table 1.

4. Case Study 2: Inversion of NCO Excited-State Potential

To extend the experience gained on the inversion procedure, a two-dimensional problem is undertaken. The experimental setup studied uses ideas from laser control employing a sequence of strong pulses, thus extending the region of inversion. In the dynamical treatment of this molecule we assume that NCO molecule is linear throughout the process. This approximation



Figure 8. Comparison of a reference potential's transient (open triangles), with the "experimental" one (dark circles). The probe wavelength for these transients is 3.37 eV.

TABLE 1: Parameters of ICN Calculations (au)

grid pulse parameters no. of expts time delay difference between expts	$\Delta R = 0.017$ $\mathbf{E} \cdot \boldsymbol{\mu} = 0.0001$ $\begin{array}{c} 60\\ \Delta t = 40 \end{array}$	fwhm = 250
------------------------------------------------------------------------------------	-------------------------------------------------------------------------------------------------------------------------	------------

facilitates the numberic calculations but otherwise is somewhat arbitrary. Having a colinear configuration, we use the the two Jacobi coordinates $r = R_{N-C}$, $R = R_{NC-O}$ to describe the dynamics where the bending motion is frozen. The Hamiltonian 2.3 is given by

$$\hat{\mathbf{H}}(t) = \begin{pmatrix} \hat{\mathbf{T}} + \hat{\mathbf{V}}_{g} & \hat{\mathbf{W}}_{ge}(t) \\ \hat{\mathbf{W}}_{eg}(t) & \hat{\mathbf{T}} + \hat{\mathbf{V}}_{e} \end{pmatrix}$$
(4.1)

where $\hat{\mathbf{T}}$ is the kinetic energy operator in Jacobi coordinates, and $\hat{\mathbf{V}}_g$ and $\hat{\mathbf{V}}_e$ are respectively the ground-state (X²Π) and excited-state (A² Σ) potential surfaces calculated by Li et al.,⁴¹ shown in Figure 9. The ground-state wave-packet mean position is at (*r*, *R*) = (2.314, 3.498) bohr, its width being (σ_r , σ_R) = (0.070, 0.065) bohr. The nondiagonal operators $\hat{\mathbf{W}}_{ge} = \hat{\mathbf{W}}^{\dagger}_{eg}$ in the Hamiltonian matrix represent the time-dependent coupling caused by the electromagnetic field of the pulses:

$$\hat{\mathbf{W}}_{\rm eg}(t) = -\hat{\mu}_{\rm eg}^* \epsilon(t) \tag{4.2}$$

Here μ_{eg} is the dipole operator, and $\epsilon(t)$ is the electric field of the pulse. This field consists of a pump pulse followed by a probe pulse. Different from the usual pump-probe experimental setups, these fields are strong and the pump pulse is not a simple pulse but a series of three Gaussian pulses, for reasons that are now discussed. The facts that the excited-state potential is strongly bound and that its minimum configuration is located close to the groundstate one mean that it is difficult to obtain a significant vibrational excitation on the excited state employing a weak-field pump pulse. This can be seen in Figure 10, where pulse 1 excites the ground-state wave packet to point a. The extent of vibrational oscillations produced on the excited surface is between points a and points b, approximately 0.2 bohr. To increase the inversion range, two extra strong pulses are used which dump and repump the wave packet.⁴² This causes a much wider range of excitation, resulting in the wave packet oscillating between points c and d. This compound pump sequence is able to attain sensitivities in a much wider range of the excited potential surface, thereby enabling meaningful inversions in extensive domains. The actual parameters concerning the three-Gaussian pump and the Gaussian probe are depicted in Table 2.



R [NC-O] (Bohr)

Figure 9. NCO potentials surfaces of the ground-state $X^2\Pi$ (top) and the excited-state $A^2\Sigma^+$ (bottom) state. The potential difference between two contour lines is 0.068 eV.

The observable of this pump-probe experiment is the residual population of the excited state. Thus the operator representing the observable is

$$\hat{\mathbf{P}}_{e} = \begin{pmatrix} 0 & 0\\ 0 & 1 \end{pmatrix} \tag{4.3}$$

Pump-probe transients are depicted in Figure 11. The grid parameters used for this (and the sensitivity function) calculation are shown in Table 3. The periodic motion of the wave packet on the excited surface is clearly observed by these transients. The nature of the wave packets motion on the excited-state potential can be traced by employing a classical trajectory. This trajectory is shown in Figure 12. The dots on the trajectory curve represent the classical predictions of the wave-packet center at the dealy times used in the inversion. It can be seen that due to the nonharmonic coupling in the potential surface, the motion corresponds to a combination of NC and CO vibrations.

The target for inversion was chosen as the excited potential, under the assumption that the ground-state potential is known to good accuracy. Thus the sensitivity functions are given by

$$\delta \hat{\mathbf{P}}_{e} / \delta V(R) = (2/\hbar) \operatorname{Im} \{ \int_{0}^{t} \chi^{*}_{e}(\tau, R) \Psi_{e}(\tau, R) \, \mathrm{d}\tau \} \quad (4.4)$$

where we assume that the NCO molecule was in its vibrational ground state prior to the interaction with the laser fields, thus $\Psi(0) = \Psi^{\circ}_{g}$ and the definitions of $\Psi_{e}(\tau)$ and $\chi_{e}(\tau)$ are

$$\Psi_{e}(\tau) = \hat{\mathbf{P}}_{e}\Psi(\tau) = \hat{\mathbf{P}}_{e}\hat{\mathbf{U}}(\tau,0) \ \Psi(0) \tag{4.5}$$

$$\chi_{e}(\tau) = \hat{\mathbf{P}}_{e}\chi(\tau) = \hat{\mathbf{P}}_{e}\chi(\tau) = \hat{\mathbf{P}}_{e}\hat{\mathbf{U}}(\tau,t) \hat{\mathbf{P}}_{e}\Psi(t) \quad (4.6)$$



Figure 10. Approximate illustration of the three-pulse pump, designed to achieve wider wave-packet oscillations on the excited potential surface. The first pulse raises 92% of the ground-state wave-packet amplitude to the excited state at point a. A second pulse carefully timed relative to the first catches the excited wave packet at point b and dumps most of its amplitude back to the ground surface, where a third delayed pulse pumps it back to the excited potential at point c. This compound pump achieves 84% excitation of the excited-state potential. For this scheme to succeed, the pulses must be strong-field π -pulses.



Figure 11. Typical NCO transients measured by the fluorescence from the $A\Sigma$ surface. For selected probe wavelengths.

 TABLE 2: Parameters of the Three-Pulse Pump and Probe for NCO Inversion (au)

parameter	pulse 1	pulse 2	pulse 3	probe
fwhm	250	250	250	250
Ε ·μ	0.009	0.009	0.009	0.009
photon energy (freq)	0.1060	0.0988	0.1131	0.100
max amplitude time	0	520	1000	0-1900
locked-phase difference	0	0	0	0

TADLE 3. Tatameters of NCO Calculations (at	TABLE 3:	Parameters	of NCO	Calculations ((au)
---------------------------------------------	----------	------------	--------	----------------	-----	---

grid	$\Delta r[N-C] = 0.028$	$\Delta R[\text{NC}-\text{O}] = 0.038$
no. of expts	80	
time delay difference	$\Delta t = 20$	
between expts		

Notice the analogy of the formalism here to that developed for the ICN molecule (see eq 3.1 to 3.6).

The sensitivity functions structures are scrutinized for the purpose of characterizing the $B_m(R)$ functions, required for inversion. Figure 13 displays sensitivity functions for various pump-probe time delays. It is clear that the sensitivity functions are relatively smooth; this is the result of the large number of pulses and the periodic motion of the wave packet



Figure 12. Classical trajectory on the excited $A\Sigma$ surface starting from the center of the excited wave function after the third pulse of the pump. The points on the trajectory correspond to time delays used for the inversion.



Figure 13. Selection of sensitivity functions for the NCO pumpprobe transient. Although smooth, these exhibit a complex structure.

on the excited surface washing out structural peculiarities. This fact suggests the use of the sensitivity functions $J_m(R)$ themselves for the targeting $B_m(R)$ functions. Indeed, this choice enabled significant inversions with initial differences between the true and the reference potentials extending to more than 0.1 eV, covering a large portion of the excited potential well bottom. Figure 14 demonstrates the inversion process at work.

5. Discussion

In this work it is demonstrated that an inversion procedure for ultrafast pump-probe experiments is feasible and advantageous, where the inversion is based on a full quantum mechanical description of the molecular dynamics.

Experience gained in many inversion attempts, most of them not described in the paper, has shown that it is common that the inversion process becomes numerically singular. This singularity is the result of overlapping sensitivity functions. To overcome this problem, numerical schemes have been employed such as the singular value decomposition. Another problem arises when the sensitivity functions have high-frequency components. This phenomena can introduce high frequencies into the inverted potential which are amplified in further



Figure 14. Progress of NCO inversion, shown on equipotential contour plots. The potential difference between two contours is 0.068 eV. The top left shows the reference potential superimposed on top of the true excited potential surface. The differences between the two reach almost 0.15 eV close to the bottom of the well. Typical evolutionary stages of the inversion are shown in subsequent plots. The time delay between two successive experiments is 0.48 fs (20 au). The probe wavelengths for each time delay is chosen as "resonance pulse", following the criterion of maximum dumping to ground state.

iterations and result in unphysical inverted potentials and severe numerical instabilities. Dealing with these cases requires special measures. In this paper we suggest the use of smooth targeting *B* functions, centered on the sensitivity functions' peak. By contrast, Ho and Rabitz²² use a Tikonov regularization, which imposes smoothness by minimizing the norm of the *n*th-order derivative of the potential.

It should be stressed that although the targeting functions approach removes the ill-posedness of the problem, the resulting linear equations can still be ill-conditioned (i.e., because of overdeterminance). Solving the ill-conditioned equations can be done in several ways. We have chosen the SVD approach, which essentially locates the minimum (L^2 norm) of the leastsquares solutions to the problem. A different approach is to use a Tikonov regularization also in this case.

Another severe problem of the inversion procedure is its nonlinearity, which demands that the initial reference potential be very close to the true potential. This is partially remedied by using features pertinent to pump-probe observables, i.e., the locality of the sensitivity functions in coordinate space and the fact that the time delay between the two pulses is a clocking device which controls the extent of sensitivity. We use these features to construct the potential in an incremental manner, starting from regions in which it is accurately known, gradually entering the unknown ones.

Considering the pump-probe inversion of Bernstein and Zewail, which used 100 fs pulses, the sensitivity functions are spread in space, smearing important details of the potential surface. We found that by decreasing the pulse widths, the sensitivity functions become narrow, more localized and together with the empirical data have higher information content concerning the potential surface peculiarities. These characteristics of course enhance the inversion capabilities. It is found that the step-by-step method follows closely the intuition and general behavior predicted by classical mechanics—features used by Bernstein and Zewail in their classical mechanical inversion.

In the NCO example a simple sequence of pump-probe pulses created sensitivity functions in a very limited region of internuclear distances. The suggested solution was to require that a more active role be played by the experimentalist and that a strong field three-pulse pump should be used to excite the molecule, thereby extending the sensitivity region. We should note here that we also tried to perform inversion (on a different system) using weak-field phase-locked pulses of identical frequencies, as suggested by Scherer et al.²⁶ We found that the sensitivity functions of the resulting observables were oscillatory, spread out over the entire inversion region, and showed a very high sensitivity to the potential. This prohibited significant inversions, since the algorithms we devised could always recover the experimental data by minute corrections to the reference potential.

It is seen in this report more than once that successful inversion demands an active role to be played by the experimentalist. This active intervention has the flavor of coherent control of molecular motion.^{17,43,44} The need for localization of the sensitivity function makes it natural to think in terms of optimal control theory, the target of which is the electromagnetic field to drive and localize the sensitivity functions in regions where the potential is vaguely known.^{42,45} For example, it is possible by chirping the pump pulse to control the width of the sensitivity. In pioneering calculations we performed on this matter, we found that this also results in diminishing the oversensitivity of the observables to the Franck–Condon region.

There is another close relation between the inversion scheme and coherent control of molecular motion. In the theory of optimal control^{17,45} the field-dependent potential is used to steer the system to a final target state. This can also be viewed as an inversion procedure where the target of inversion is the field and the target state plays the role of the measurement. This similarity can be traced by comparing the first order perturbation control equation of Yan et al.⁴⁶ and eq 2.38.

Acknowledgment. It is a pleasure to thank David Tannor Sandy Ruhman and Stuart Rice for active encouragement and discussions. This research was supported by the Binational United States—Israel Science Foundation. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, GmbH München, FRG.

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JP941301W