Obtaining the excited-state potential by inversion of photodissociation absorption spectra

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An inversion scheme to obtain excited-state potential energy surfaces from experimental absorption spectra is presented. The scheme is based on simulating the quantum dynamical processes with high accuracy. A modification of the simulation enables analysis of regions in the potential which the absorption spectrum is sensitive to. These sensitivity regions are then used to construct a Hilbert space which becomes the functional base for the inversion procedure. In this Hilbert space an iterative scheme converges an initial model to a new potential which will reproduce the spectra. The scheme is illustrated for the ICN molecule.

1. Introduction

Spectroscopic measurements have been extremely important in probing the structure and dynamics of molecules. The concepts elucidating the dynamics are based on the adiabatic theorem where the nuclear motion is slow compared to the motion of the underlying electrons. In the resulting picture, the adiabatic eigenvalues of the electronic wavefunction construct the potential energy surface (PES) on which nuclear motion takes place [1]. The different bands in the absorption spectra can be assigned to transitions from the ground surface to different excited potential energy surfaces. One step further in the analysis is to obtain the form of the excited PES which is responsible for the shape of the absorption band. The task is a classical example of an inversion procedure from which the form of the potential influencing the measurement is to be inferred.

The weakness of the inversion process is that more than one possible potential can faithfully reproduce the measurement so that additional assumptions have to be added. In the theory of mathematical inversion these assumptions usually impose analytic properties on the potential as well as an asymptotic van-

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ishing of the potential and its derivatives for large internuclear distances R. Even under such stringent conditions mathematical inversion procedures are limited to one effective dimension, because the large degree of over-determination in higher dimensions. A good summary of inversion of scattering data is found in the book by Newton [2].

The semiclassical RKR method is most widely used to invert spectroscopic data [3,4]. The method is based on locating the distance between the inner and outer classical turning points of the potential. The inversion demonstrates the principle that there are infinitely many potentials which are able to reconstruct the experiment, since a mapping of the potential that preserves the action between the two turning points will produce the same observed spectrum [5]. An exception to the one-dimensional inversion procedures has been developed by Gerber and Ratner [6,7], The main idea is to use a self-consistent field (SCF) procedure to break the multidimensional space into a set of one-dimensional coupled systems. They are then inverted by the RKR method sequentially and an iterative procedure is used to solve the self-consistent set of coupled equations.

The difficulty in direct inversion procedures has led to the use of heuristic indirect procedures. They are based on solving the dynamics by using a model potential. The outcome of the modeling is first compared to the measurement. Then the potential is altered and the modeling run again until a satisfactory comparison between the model and the experimental data is obtained. One drawback of the heuristic approach is that it is arbitrary-dependent on the functional form of the potential chosen for the modeling. Another drawback is that the heuristic approach does not have systematic convergence properties.

This Letter presents an iterative procedure for potential inversion from absorption spectra. In order to overcome the arbitrariness of the procedure, all available information as well as intuition on the form of the excited-state potential is utilized to construct an initial guess. The iterative procedure alters numerically the initial guess of the potential until the experiment measurements are reconstructed. In this way the inverted potential is as close as possible to the initial assumptions circumventing therefore, the nonuniqueness of the inversion procedure. For example, the initial guess can be an ab initio calculated potential.

Starting from the initial guess for the potential, the first step is to map out the regions of the potential to which the measurements are sensitive. The basic tools are high quality quantum mechanical methods for simulating the experiment. For dynamical molecular processes, the combination of the Fourier grid representation of the wavefunction with the Chebychev polynomial expansion of the evolution operator, have been shown to provide extremely accurate and stable results [8–12]. In particular, these methods can be extended to calculate directly the absorption [10] or Raman spectra [9] of weak field excitation.

Based on high quality simulations, the sensitivity of the observation to a small variation in the potential can be studied. These sensitivity functions are the starting point of the inversion procedure. Small variations in the potential suggest that a perturbative approach based on a zero-order Hamiltonian can be used. A perturbation based inversion scheme for spectroscopic measurements has been worked out by Kosman and Hinze [13]. Sensitivity analysis of dynamical processes has been extensively studied by Rabitz and co-workers [15]. Based on their analysis Ho and Rabitz have developed a potential inversion scheme for inelastic scattering experiments [16] and for vibration-rotational line spectra [17]. The inversion schemes in this paper are based on high quality quantum simulations which are able to simulate faithfully the experiment and obtain the sensitivity functions. Based on these sensitivity functions an orthogonal functional space is constructed which is the main tool of the inversion process.

The method used in the present work is closely related to the approach of Ho and Rabitz [15-17]. The high quality simulations which are obtained from the time-dependent quantum mechanical approach enable inversion of a large body of experimental data. The original motivation was to construct a time-dependent quantum mechanical inversion scheme to replace the classically based inversion scheme for a pump-probe photodissociation experiment suggested by Bernstein and Zewail [18]. Although such a classical inversion scheme has been criticized by Krause et al. [19] preliminary studies have shown that a full quantum potential inversion of pumpprobe experiments is possible [20]. Since it was found that the pump-probe experiment has extreme sensitivity to the Frank-Condon region of the potential, this region has to be determined from other experiments. For this reason the time-dependent inversion scheme from absorption spectra of photodissociating molecules was developed.

2. Weak field absorption spectra

The simplest electronic absorption dynamics involving two surfaces can be followed by solving the time-dependent Schrödinger equation for two coupled electronic surfaces and by a semiclassical description of the electromagnetic field:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_{g} \\ \psi_{e} \end{pmatrix} = \begin{pmatrix} \hat{H}_{g} & -\hat{\mu}\epsilon \\ -\hat{\mu}\epsilon^{*} & \hat{H}_{e} \end{pmatrix} \begin{pmatrix} \psi_{g} \\ \psi_{e} \end{pmatrix}, \qquad (1)$$

where

$$\hat{H}_i = -\frac{\hbar^2 \nabla^2}{2\mu} + \hat{V}_i(\hat{r}) .$$
⁽²⁾

The index *i* is the molecular ground/upper surface field-free Hamiltonian, $\hat{\mu}(r)$ is the dipole operator, and $\epsilon(t)$ is the radiation field. A semiclassical $\mu\epsilon$ field interaction is used. In the spectroscopic measure-

ment the Schrödinger equation is subject to the condition in which all of the initial amplitude is in the ground surface:

$$\Psi(0) = \begin{pmatrix} \psi_{\mathbf{g}}(0) \\ 0 \end{pmatrix}. \tag{3}$$

The absorption spectra measurement is based on determining the balance of energy absorbed from the electromagnetic field and dissipated by the molecule. From eq. (1) the power or the rate of energy change at time t is calculated:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \left\langle \frac{\partial \hat{H}}{\partial t} \right\rangle = -2 \operatorname{Re}\left(\left\langle \psi_{g} | \hat{\mu} | \psi_{e} \right\rangle \frac{\partial \epsilon}{\partial t} \right).$$
(4)

The first equality is the result of the commutation of the Hamiltonian with itself while the second equality exists because the only part of the Hamiltonian which is time dependent is the field $\epsilon(t)$. In a common type absorption experiment the field can be described by the rotating frame wave form:

$$\epsilon(t) = \frac{1}{2}A(t)e^{i\omega t}, \qquad (5)$$

where A(t) is a slowly varying envelope function turned on at t=0. For this pulse the instantaneous power becomes

$$\frac{dE}{dt} = 2\omega \operatorname{Im}\left[\langle \psi_{g}(t) | \hat{\mu} | \psi_{e}(t) \rangle \epsilon\right] -2 \operatorname{Re}\left(\langle \psi_{g}(t) | \hat{\mu} | \psi_{e}(t) \rangle \frac{\dot{A}}{A} \epsilon\right).$$
(6)

The measured quantity is the average power, and therefore eq. (6) has to be averaged for the duration of the pulse,

$$\bar{P}(\omega, t) = \frac{1}{t} \int_{0}^{t} \frac{dE}{d\tau} dt$$
$$= 2 \frac{\omega}{t} \operatorname{Re} \int_{0}^{t} A(\tau) \langle \psi_{g}(\tau) | \hat{\mu} | \psi_{e}(\tau) \rangle e^{i\omega\tau} d\tau, \quad (7)$$

where, because A is a slowly varying envelope function, $\dot{A}/A \ll \omega$, which leads to neglecting the term proportional to \dot{A} in eq. (6). Eq. (7) is correct for all field strengths, and can be used as the starting point for the inversion since it constitutes an explicit relation between the dynamics of the system and the averaged power which is an observed quantity. Eq. (7) can be used directly although what is more common is to extend the integration to $t \rightarrow \infty$, and to normalize to the total energy carried by the light pulse.

In weak field conditions, the expression for the power can be simplified by using the assumption that the evolution of the wavefunction on the ground surface is not altered by the field, leading to

$$\psi_{\mathbf{g}}(t) \approx \psi_{\mathbf{g}}(0) \mathbf{e}^{-i\omega_0 t} \,, \tag{8}$$

where $\hbar\omega_0$ is the ground state energy. The excited state wavefunction can be obtained by integrating equation (1):

$$\psi_{e}(t) = \frac{i}{\hbar} \int_{0}^{t} d\tau \exp\left(-\frac{i}{\hbar} \hat{H}_{e}(t-\tau)\right)$$
$$\times \hat{\mu} \epsilon^{*}(\tau) \psi_{g}(\tau) . \tag{9}$$

With the use of the time-dependent first-order perturbation theory, one obtains

$$\psi_{e}(t) \approx \frac{i}{\hbar} \int_{0}^{t} d\tau \exp\left(-\frac{i}{\hbar} \hat{H}_{e}(t-\tau)\right)$$
$$\times \hat{\mu} \epsilon^{*}(\tau) \psi_{g}(0) e^{-i\omega_{0}\tau}.$$
(10)

Assuming that the envelope function is almost time independent and proportional to E_0 , the average field intensity, and taking into account eqs. (8) and (10), one obtains a steady state expression for the power absorbed [21]:

$$\overline{P}(\omega, t) = \omega B \int_{-t}^{t} d\tau \exp\left[i(\omega + \omega_0)\tau\right]$$
$$\times \langle \theta_0 | \exp\left(-\frac{i}{\hbar}\hat{H}_e\tau\right) | \theta_0 \rangle, \qquad (11)$$

where the following symbols are used:

$$\theta_0 = \hat{\mu} \psi_{\mathbf{g}}(0) , \qquad (12)$$

and $B = |E_0|^2/4\hbar$. Eq. (12) is interpreted as if the dynamics of a new wavefunction θ_0 is generated by the excited state Hamiltonian \hat{H}_e . This expression, which is the starting point of the weak field inversion, since it relates the observation to the dynamics, has been obtained by Heller [22].

3. Sensitivity of the absorption spectrum to the molecular potential surface

The first step in the inversion is to study the observation sensitivity to the excited surface potential contained in H_e (the standard form is assumed $H_e = T + V_e$). Calculating the first-order variation of the excited state evolution operator to a variation in the potential one obtains

$$i\hbar \,\delta \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_{\mathrm{e}}t\right) = \int_{0}^{1} \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_{\mathrm{e}}(t-\tau)\right)$$
$$\times \delta\hat{V}_{\mathrm{e}} \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}_{\mathrm{e}}\tau\right) \mathrm{d}\tau, \qquad (13)$$

From eq. (13) the sensitivity of the absorption spectrum to a variation in the excited state potential can be obtained:

$$i\hbar \,\delta \bar{P}(\omega, t) = \omega B \int_{-t}^{t} d\tau \exp[i(\omega + \omega_0)\tau]$$

$$\times \int_{0}^{\tau} dt' \langle \theta_0 | \exp\left(-\frac{i}{\hbar} H_e(\tau - t')\right)$$

$$\times \delta \hat{V}_e \exp\left(-\frac{i}{\hbar} H_e t'\right) | \theta_0 \rangle. \qquad (14)$$

On changing to coordinate representation

$$i\hbar \,\delta \bar{P}(\omega, t) = \omega B \int_{-t}^{t} d\tau \exp[i(\omega + \omega_0)\tau]$$

$$\times \int_{0}^{\tau} dt' \int dR \,\theta^*(t' - \tau, R) \,\delta V_e(R) \,\theta(t', R) \quad (15)$$

(where $\theta(t) = \hat{U}(t, 0)\theta_0$). The functional derivative describing the sensitivity becomes

$$\frac{\delta \bar{P}(\omega, t)}{\delta V_e(R)} = \frac{\omega B}{i\hbar} \int_{-t}^{t} d\tau \exp[i(\omega + \omega_0)\tau] \times \int_{0}^{\tau} dt' \,\theta^*(t' - \tau, R)\theta(t', R) \,. \tag{16}$$

This is the desired expression for the sensitivity of the absorption rate to the excited-state potential V_{e} .

To numerically evaluate eq. (16) the wavefunction is propagated by using the Chebychev expansion of the evolution operator $\hat{U}(t, 0)$ [9]:

$$\theta(t) = \hat{U}(t,0) \ \theta(0) \approx e^{i\hat{\omega}t} \sum_{n=0}^{N} a_n(\nu t) \phi_n .$$
 (17)

Here, $a_n = (2 - \delta_{n0})J_n$, where J_n are the Bessel functions, ϕ_n is the result of operating with the Chebychev polynomial operator $T_n(\hat{H}_N)$ on θ_0 and \hat{H}_N is the normalized Hamiltonian $\hat{H}_N = (2\hat{H} - \hat{\omega})/\nu$, where

$$\nu = \frac{E_{\max} - E_{\min}}{2\hbar}, \quad \hat{\omega} = \nu + \frac{E_{\min}}{\hbar}, \quad (18)$$

and ϕ_n are calculated by the recursion relation of the Chebychev polynomial: $\phi_0 = \theta_0$, $\phi_1 = -i\hat{H}_N\phi_0$ and $\phi_{n+1} = -2i\hat{H}_N\phi_n + \phi_{n-1}$. Inserting eq. (17) into equation (16) leads to a double sum of a product of terms which can be evaluated using the following identities for the Bessel functions:

$$\int_{0}^{\tau} dt' J_{n}(\tau - t') J_{m}(t')$$

= $2 \sum_{\kappa=0}^{\infty} (-1)^{\kappa} J_{n+m+2\kappa+1}(\tau)$ (19)

and

$$J_n(-t) = (-1)^n J_n(t) ,$$

with the result

$$\frac{\delta \bar{P}(\omega,t)}{\delta V_{e}(R)} = \frac{2\omega B}{i\hbar\nu} \sum_{n=0}^{N} \sum_{m=0}^{N} (-1)^{n} (2-\delta_{m,0}) (2-\delta_{n,0})$$
$$\times r_{m+n}(\omega+\omega_{0}+\hat{\omega},\nu,t)\phi_{n}^{*}(R)\phi_{m}(R) , \qquad (20)$$

where

$$r_{s}(\omega, \nu, t) \equiv \int_{-t}^{t} d\tau e^{i\omega\tau} \sum_{\kappa=0}^{\infty} (-1)^{\kappa} J_{s+2\kappa+1}(\nu\tau),$$

$$s=0, ..., 2N.$$

Caution should be taken in making use of the limit $t \rightarrow \infty$ in eq. (20) because the finite Chebychev expansion applies only to finite times since the integral in eq. (20) diverges as t approaches infinity. This is in accordance with the observation that any spectroscopic measurement is completed in finite time,

either because of a finite pulse length, or because of fluctuations in the light source which effectively limit the observation time.

4. Inversion in sensitivity space

Practically, a measurement of the absorption spectrum consists of a series of N measurements where the frequency ω_i is varied and the power absorbed $\bar{P}(\omega_i, t)$ is registered. This measured value as discussed in section 3, is a functional of the true excited state potential: $\bar{P}[\hat{V}_e^{\text{true}}]$. Assuming a model potential \hat{V}_e^A is a good approximation to the true potential such that the difference

$$\delta \hat{V} = \hat{V}^{\text{true}} - \hat{V}^{\text{A}} \tag{21}$$

is small, the experimental results are used to improve the approximation iteratively. The deviation $\delta \hat{V}$ from the true potential introduces a variation in the absorption spectrum $\delta \bar{P}(\omega_i, t)$ of the *i*th experiment with central frequency ω_i . This is given up to first order by

$$\delta \bar{P}(\omega_i, t) \equiv \bar{P}[\hat{V}_e^{\text{true}}] - \bar{P}[\hat{V}_e^{\text{A}}]$$

$$= \int_R \frac{\delta \bar{P}(\omega_i, t)}{\delta V} \Big|_{V^{\text{A}}} \delta V(R) \, \mathrm{d}R$$

$$= \int_R \sigma_i(R) \, \delta V(R) \, \mathrm{d}R = (\sigma_i, \delta V) \,, \qquad (22)$$

where σ_i is the sensitivity of $\bar{P}(\omega_i, t)$ to the potential V^A . Since only the coordinate representation of the potential is considered its operator notation has been omitted. At this point the sensitivity Hilbert space is defined by the inner product:

$$(f,g) = \int_R f(R)g(R) \,\mathrm{d}R \;.$$

The integration domain is chosen so that the measured value is insensitive to the variation of V outside of this domain and $\sigma_i(R) = 0$ for R outside the domain.

To avoid problems of overdetermination, the set of sensitivity functions $[\sigma_i]_{i=1}^N$ is orthonormalized with respect to the inner product (f, g). The procedure creates N new observables:

$$I_i = \sum_{j=1}^{N} c_{ij} \bar{P}(\omega_j, t) , \qquad (23)$$

and their sensitivity functions

$$S_i = \sum_{j=1}^N c_{ij}\sigma_j$$

so that the inner product $(S_i, S_j) = \delta_{ij}$. Because of the linearity of the inner product and the orthogonal relation,

$$\delta I_i = (S_i, \delta V) . \tag{24}$$

This means that the orthogonal set of experimental sensitivity functions $\{S_i\}$ can be used to expand the variation δV :

$$\delta V = \sum_{i=1}^{N} S_i(S_i, \delta V) + \delta V^{\text{ortho}}, \qquad (25)$$

where $\delta \hat{V}^{\text{ortho}}$ is the part of $\delta \hat{V}$ which is orthogonal to the space spanned by S_i . Using the definition of the deviation of the orthogonal set of observations in eq. (24),

$$\delta V = \sum_{i=1}^{N} S_i \, \delta I_i + \delta V^{\text{ortho}} \tag{26}$$

is obtained. The equation relates δV , the correction to the approximated potential V^A , to δI_{j} , the deviation of the calculated orthonormal observations from their measured values. It is clear that once the approximate potential $V^A(R)$ and the observables have been given the solution is optimal since the orthogonal part cannot be controlled by the set of observables. Eq. (26) is the base of the iterative procedure where the potential is systematically corrected until the deviations of the set of orthogonal observations is below a certain tolerance (usually related to the experimental error).

5. Illustrative examples

The absorption spectrum of ICN in the A band was chosen as an illustrative example of the inversion procedure. Reviewing the literature on the ICN system one finds that both the experimental and theoretical interpretation of the absorption to the A band of ICN are under dispute [23-29]. This is because more than one excited potential energy surface can be involved in the absorption process. Also the contributions of the CN bend and stretch modes to the spectrum have been ignored. Since the purpose of this work is to demonstrate the inversion procedure it is assumed that the experimental absorption spectrum is given by the data of Hess et al. [24] shown in fig. 1. It is also assumed that the transition takes place to predominantly one excited surface that is the target of the inversion. The asymmetrical experimental spectrum is poorly approximated by the semiclassical formula

$$\vec{P}(\omega) \propto \exp\left(-\frac{(\omega-\omega_0)^2}{\sigma^2 \alpha^2}\right), \qquad (27)$$

where $\sigma^2 = \hbar/m\omega_g$ and $\alpha = -\hbar^{-1}dV(R)/dR|_{Req}$. This means that a linear potential is not adequate. Two initial models for the excited state potential are considered. The first is the potential fitted by Goldfield et al. [26] and the second is the ab initio potential of Yabushita et al. [27]. The simulated absorption spectra obtained from these two potentials are superimposed on the experimental spectrum shown in fig. 1.

As discussed in section 3, the first step in the inversion is to calculate the sensitivity functions. To



Fig. 1. The absorption spectra of ICN by Hess et al. [24] (solid line), Pitts et al. [23] (dotted line). Superimposed are the simulated absorption spectra using the potentials of Goldfield et al. [26] (broken line) and Yabushita et al. [27] (thin solid line).

overcome experimental problems, the spectrum is normalized to its maximum. This means a slight modification in the observable used for the inversion which becomes $\bar{P_i}/\bar{P_{max}}$, with its accompanying sensitivity:

$$\frac{\delta(\bar{P}_i/\bar{P}_{\max})}{\delta V(R)} = \frac{\sigma_i}{\bar{P}_{\max}} - \frac{\bar{P}_i \sigma_{\max}}{\bar{P}_{\max}^2}, \qquad (28)$$

where σ_i is defined in eq. (22) and is calculated using the model potentials of ref. [26] and eq. (20). The sensitivity functions are displayed in fig. 2. The initial wavefunction $\psi_g(0)$ was calculated by propagating an initial guess on the ground surface in imaginary time until convergence to the ground state was obtained [30]. Note that the first peak of the sensitivity function is shifted to larger internuclear distances with decreasing frequency. This is in accordance with the Frank-Condon principle. Notice that the sensitivity functions have a long oscillating tail downhill from the Frank-Condon point. After the raw sensitivity functions are calculated a Gramm-Schmidt orthogonalization procedure is used to obtain an orthogonal set.

Once a base for the Hilbert space of the inversion domain has been constructed the iterative inversion procedure can proceed. Using eq. (25) a systematic improvement in the potential is obtained. A smoothing filter was applied to the correction which was gradually removed. Such a procedure is different from the regularization procedure used by Ho and Rabitz [16]. Without the filter the converged po-



Fig. 2. Sensitivity functions of the absorption spectra as a function of internuclear distance R for different excitation frequencies.

tential was found to have oscillations. Fig. 3 shows a series of potentials where the last converged potential reconstructs the experimental spectra within a tolerance of 10^{-15} (20 sampling points from the absorption spectra were used for the inversion). The procedure was applied to the two model potentials until convergence was obtained. The results are displayed in fig. 3. The converged potentials are not affected outside the Frank-Condon region and have different asymptotic behavior. The potential of Yabushita et al. has a lower dissociation energy and is less steep for small *R*.

The converged results can shed some light on the form of the excited surface. Although the calcula-



Fig. 3. (a) Convergence of the ICN potentials starting from the potential of Goldfield et al. [26] (dotted line). The dashed line is the second iteration with a significant smoothing filter on the corrections. The solid line is the converged result where the filter is absent. (b) The same as (a) for the potential of Yabushita et al. [27].

tions are one dimensional the calculated spectrum fits quite well to the two-dimensional results of Lee [29]. This is because the bending degree of freedom does not have enough time to develop before the decay of the autocorrelation function (≈ 2 fs). It is clear that both model potentials are shifted to the blue. Also the converged potential has become steeper in the Frank-Condon region.

6. Discussion and summary

The nonuniqueness of the inversion process is clearly demonstrated in fig. 4, where starting from two different models two final converged potentials reconstruct faithfully the absorption spectra. Because of this nonuniqueness results can be obtained only within a specific model of the dynamical process. Since intuitively smooth potentials are preferable, the method incorporates a bias toward smooth potentials. Even this bias does not overcome the uniqueness problem. Does this mean that the inversion effort is meaningless? The real benefit of procedure are the guidelines set by the sensitivity functions on the amount of useful information which can be gained by present and future experiments. Summarizing, it should be emphasized that the potential that reproduces the experiment is only one out of infinitely many possibilities. Additional experiments



Fig. 4. The converged potentials starting from two different initial guesses. The dashed line started from the potential of Goldfield et al. [26] and the dotted line started from the potential of Yabushita et al. [27].

of the same type will not help since the sensitivity analysis determines the number of really independent experimental points. To nail down further the potential a different type of experimental observation should be employed for which the sensitivity functions are orthogonal to the previous set of experiments. For example, a Raman experiment. For the Raman cross section

$$\sigma_{if} = A\omega_{s}^{3}\omega_{L}$$

$$\times \left| \int_{0}^{\infty} dt \langle f | i(t) \rangle \exp[i(\omega_{L} + \omega_{i})t] \right|^{2}$$

$$= A\omega_{s}^{3}\omega_{L}FF^{*} \qquad (29)$$

the sensitivity function becomes

$$\frac{\delta\sigma_{ij}}{\delta V(R)} = A\omega_5^3 \omega_L \left(\frac{\delta F}{\delta V(R)}F^* + \text{c.c.}\right), \tag{30}$$

where

$$\frac{\delta F}{\delta V(R)} = \frac{1}{i\hbar} \int_{0}^{t} d\tau \exp[i(\omega_{\rm L} + \omega_{\rm i})\tau]$$
$$\times \int_{0}^{\tau} f^{*}(t' - \tau, R)i(t', R) dt'$$

and i(0) and f(0) are the initial and final eigenfunctions respectively. This equation can be evaluated by using the Chebychev expansion of the evolution operator leading to

$$\frac{\delta\sigma_{ij}}{\delta V(R)} = \frac{2A\omega_{\rm S}^3\omega_i}{i\hbar\nu} \sum_{n=0}^N \sum_{m=0}^N (-1)^n (2-\delta_{m,0})$$

$$\times (2-\delta_{n,0})r_{m+n}(\omega+\omega_0+\hat{\omega},\nu,t)\phi_n^*(R)\psi_m(R)F^*$$
+c.c., (31)

where

$$r_{s}(\omega, \nu, t) \equiv \int_{0}^{t} \mathrm{d}\tau \,\mathrm{e}^{\mathrm{i}\omega\tau} \sum_{\kappa=0}^{\infty} (-1)^{\kappa} J_{s+2\kappa+1}(\nu\tau),$$

$$s=0, \dots, 2N.$$

and $\psi_n = T_n(\hat{H}_e)f(0)$ and $\phi_n = T_n(\hat{H}_g)i(0)$. The sensitivity function of the Raman process is shifted to larger internuclear distances thus increasing the observation window on the excited potential energy

surface. The pump-probe experiment [18] increases the observation window even further.

The approach presented in this work is part of a larger effort to establish iterative schemes for inferring potential energy surfaces from experimental observations. The idea is to guide the experimentalist by setting experiments which have maximum information content with minimum overlap between them. This can be done because the sensitivity space is common to all experiments. The procedure is then refined with the guidance of the new experimental data and iteratively continued until convergence. Such an approach was suggested also by Wilson in a sketch of a controlled spectrometer [31].

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