Validation of photodissociation models using Raman excitation Profiles: an application to IBr

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Abstract

The validity of different sets of model potential energy curves and functional forms for nonadiabatic and optical coupling between them used to treat IBr photodissociation is ascertained by calculation of Raman excitation profiles using the time dependent wave packet method. Our results suggest that the additional three states in the six state model play only a marginal role in the photodynamics of IBr.

1. Introduction

Resonance Raman spectroscopy has emerged as a powerful and sensitive probe for deciphering the detailed dynamics of chemical reactions [1]. Resonance Raman intensities observed at different excitation wavelengths, termed as Raman excitation profiles (REPs) have been shown to be particularly sensitive to minor variations in the underlying potential energy curves and coupling elements controlling the photodynamics of a system [2–5].

IBr has served as a prototype for detailed theoretical investigation and possible selective control of photodissociation processes [6–9]. The investigations however have employed different sets of potential energy curves and non-adiabatic/optical coupling matrix elements, with the six state model of Levy et al. [9] being the most comprehensive. The three state model employed by Gross et al. [7] for optimal control and by Bairagi et al. [8] for field optimized initial state (FOIST) based selective control of IBr photodissociation products has however captured the essential photodynamical features quite adequately. An even simpler three state model with only one optically coupled excited state and a constant nonadiabatic coupling matrix element between the two excited states has been employed by Guo [4], who calculated both photoabsorption spectrum and REP for IBr utilizing a spatial grid consisting of only 512 grid points.

Due to the large reduced mass of IBr and importance of much slower predissociation in its photodynamics, the wavepacket on the excited state can be highly delocalized and most calculations routinely employ 1024 spatial grid points. The use of six state model for treating IBr photodissociation, therefore, is computationally demanding and it is desirable to investigate if the more economic three state model is adequate to reproduce the essential features of IBr photodynamics. Since REPs are sensitive to even minor systemic details, their calculation using both the three and the six state models and a comparative
analysis of the results can provide a sensitive probe for investigating the adequacy of the three / six state IBr models. The time-dependent wave packet (TDWP) calculation of the IBr REPs have been carried out earlier by Guo [4]. His calculations, however, utilized many approximations mentioned earlier. Furthermore, the three state model of Guo gives REPs that are structureless in the direct dissociation (λ < 548 nm, the Br + I dissociation limit) region, while the first order perturbation theoretic calculations of Levy et al. [9] yield structures that have been utilized to deduce that the REPs retain the memory of the final vibrational state.

It is therefore useful to calculate the IBr REPs accurately using both the three and the six state models to investigate the competing dynamic effects from different states and to ascertain if the more accurate TDWP calculations undertaken here using the same states and couplings as those employed by Levy et al. [9] can reproduce the structure seen in the REP in the direct dissociation regime (λ < 548 nm). These calculations should also provide a rigorous assessment of the comparative adequacy of the more economic three state model for IBr photodissociation, so that, if the three state model is found to be sufficiently accurate, it may be employed routinely to provide substantial computational economy without sacrificing the essential features of the photody-

Fig. 1. (a) IBr Potential energy curves. [0 : \( \chi^3 \Sigma_0^+ \), 1 : \( \chi^1 \Pi_1 \), 2 : \( \nu(\Pi_{\nu \nu}) \), 3 : \( \nu(\Pi_{\nu \nu}) \), 4 : \( \nu(\Pi_{\nu \nu}) \) and 5 : \( \nu(\Pi_{\nu \nu}) \)]. (b) Total autocorrelation function \( C_{\nu\nu}(\tau) \times 10^\frac{2}{2} \) from the three (---) and the six (...) state models. (c) Total cross-correlation function \( C_{\nu\nu}(\tau) \times 10^\frac{2}{2} \) from the three and the six state models. (d) Total absorption spectrum \( \sigma_\nu(\lambda) \) from the three and the six state models.
namics. In view of the strong interference effects seen in the continuum Raman REPs [1,5,9–11] and close proximity of the additional curves in the six state model such an investigation for IBr assumes added significance.

2. Method

In the time-dependent wave packet method, the Schrödinger equation is solved with $|\phi'(0)\rangle = \mu_{0\ell}|\psi_0\rangle$, where $\psi_0$ is the initial ground state wavefunction and $\mu_{0\ell}$, the transition dipole moment between the ground and the $\ell$th excited state. The time evolution of the promoted state wavefunction is described by

$$|\phi'(t)\rangle = \exp(-iH_{ex}t/\hbar)|\phi'(0)\rangle,$$

(1)

where $H_{ex}$ is the excited state Hamiltonian [10–13]. The overlap of the time evolving wavefunction $\phi'(t)$ with the initial promoted state wave function $\phi'(0)$ is the autocorrelation function $C_{00}(t) = \langle \phi'(0)|\phi'(t)\rangle$ and is a measure of how fast the promoted state leaves the Franck-Condon region [10,14,15]. The total autocorrelation function is the

Fig. 2. (a–d) Raman excitation profile for the fundamental and overtones for IBr from both the three and the six state models.
sum of the individual autocorrelation functions for different channels and is given by,
\[ C_{00}(t) = \sum_{\ell} C_{00}^{\ell}(t). \]  
(2)

Fourier transform of the individual autocorrelation functions yields the partial absorption cross sections [13]:
\[ \sigma_\ell(\omega) \propto \omega \int_{-\infty}^{\infty} C_{00}^{\ell}(t) e^{i(\omega + \omega_0)t} dt, \]  
(3)

where \( \omega \) is the frequency of the incident laser and \( \hbar \omega_0 \) is the energy of the initial ground state \( \psi_0 \). Total absorption cross section is a sum of the partial absorption cross sections:
\[ \sigma(\omega) = \sum_{\ell} \sigma_\ell(\omega). \]  
(4)

The overlap of the final vibrational wavefunction (on the ground electronic state) with the time evolving promoted state wavefunction (on the excited state) \( C_{00}^{\ell}(t) = \langle \psi_f(0) | \psi^{\ell}(t) \rangle \) is termed the cross-correlation or Raman correlation function [10–19] and for Raman intensity analysis, the Raman amplitude \( \alpha_{00}(\omega) \) for each channel is obtained from the corresponding Raman correlation function:
\[ \alpha_{00}(\omega) = (i/\hbar) \int_{0}^{\infty} C_{00}^{\ell}(t) e^{i(\omega + \omega_0)t} dt, \]  
(5)

and the Raman excitation profile from the Raman amplitude:
\[ I_{00}(\omega) = \omega \omega_0 \cdot |\alpha_{00}(\omega)|^2, \]  
(6)

with \( \omega_0 \) being the frequency of the scattered radiation. The total observable Raman intensity \( I_{00}(\omega) \) is computed from the total Raman amplitude, which is a sum of the partial Raman amplitudes:
\[ I_{00}(\omega) = \omega \omega_0 \cdot |\alpha_{00}(\omega)|^2 = \omega \omega_0 \cdot |\sum \alpha_{00}(\omega)|^2. \]  
(7)

Interference among the Raman amplitudes \( \alpha_{00}(\omega) \) corresponding to different channels results in structures in the total Raman intensity profile.

Vibrational eigenfunctions \( \psi_f \) and the corresponding eigenvalues for I\( \text{Br} \) in its ground electronic state

![Fig. 3. Norm of the wavefunction as a function of time on different excited states in the three and the six state models.](image-url)
have been calculated using the Fourier grid Hamiltonian method [20]. The split-operator fast Fourier transform (SOFFT) algorithm [21–24] was utilized to integrate the time-dependent Schrödinger equation. A total spatial grid of 14 a₀ (2–16 a₀) was used in IBr bond length and it was divided into 1024 equally spaced grid points. A linear ramp (optical potential) with a maximum height of 0.01 Hartree was set up near the edge of the grid ranging from 14.85 a₀ to 16.0 a₀. The wavefunction was propagated on the excited states for a total of 8192 fs (T) in time steps of 0.5 fs each providing a resolution (∼2π/T) of 5.1 × 10⁻² eV or 4.1 cm⁻¹.

3. Results and discussion

Potential energy curves used for IBr [0 : X₁Σ⁺, 1 : A(Π₁), 2 : B(Π₁), 3 : Y(0⁺), 4 : Y’(0⁺) and 5 : B’(Π₁)] are plotted in Fig. 1a and the systemic parameters are those tabulated in Ref. [9]. The three state model is a truncation, where only the ground state X₁Σ⁺, and the second and the third excited states B(Π₁) and Y(0⁺) respectively are retained. To ensure a proper comparison between the three and the six state models, same systemic parameters for both the sets have been used, i.e. the three state model is a subset of the six state model. The nonadi-

Fig. 4. Partial contributions \( I_{\lambda}(\lambda) \) from individual excited states to the fundamental Raman excitation profile \( I_{\lambda}(\lambda) \). The dominant role of the \( B(Π₁) \) state is clearly seen.
abatic and dipole coupling matrix elements used by Guo are different, yet the IBr REPs reported in his work [4] are comparable to the three state results presented here.

The autocorrelation function and cross correlation function for the fundamental Stokes line from the three and six state models and the corresponding absorption spectra are plotted in Figs. 1b, 1c and 1d, respectively. The value of $C_{00}(t)$ at $t = 0$ from the two models represents the sum $|\mu_{02}|^2 + |\mu_{03}|^2$ and $\sum_{\gamma=1}^5 |\mu_{0\gamma}|^2$, respectively. The $C_{00}(t)$ from both the models have essentially the same form and decay time. This similarity between results from the two models persists in the case of the cross-correlation function (Fig. 1c) and also the computed absorption spectra (Fig. 1d). The latter follow closely the experimental absorption spectrum [9]. The absorption spectra from the two models differ in the predissociative regime, where, as expected, the presence of the lower lying excited state $A(^1\Pi_1)$ in the six state model leads to the longer wavelength structure missing in the three state model.

The REPs obtained from both the models are structureless in the direct dissociation region ($\lambda = 400–540$ nm) and are reproduced only for the fundamental in the insets of Fig. 2a. These are however similar to each other, decrease progressively for higher overtones and do not mirror the topology of

![Fig. 5. Partial contributions $\sigma_i(\lambda)$ from individual excited states to the absorption spectrum $\sigma(\lambda)$, as obtained from the three and the six state models. The $B(^1\Pi_1)$ state makes the dominant contribution.](image-url)
the final vibrational state wavefunctions. The REP in the range $\lambda = 540-590$ nm for the overtones are shown in Figs. 2b–2d. Results from the two models differ from each other. Those from the six state model with a larger number of channels for the leakage of the initial amplitude are smaller in magnitude in comparison to that from the three state model. This assertion is buttressed by Fig. 3a and Fig. 3b, wherein we have plotted the evolution of probability density for each excited state as a function of time. It is clear from Figs. 3a and 3b that the depletion of norm is larger in the six state model due to the availability of extra pathways offered by the additional states. The six state model yields some additional long wavelength peaks due to the lower lying $\Pi_3^0$ state. The decrease in intensity of the REP peaks from the six state model is similar to that seen for REPs calculated by including nonadiabatic coupling between the $B(\Pi_3^0)$ and $Y(\Omega^+)$ states in Guo’s work [4] in which the presence of nonadiabatic coupling diminished the intensity pattern when compared to the REPs calculated without including the nonadiabatic coupling.

The partial REPs from each excited state in both the models are plotted in Fig. 4. They are completely determined by the optically brightest $\Pi_3^0$ state in both the models. The other states seem only to be additional outlets for funnelling amplitude away from the brightest state thereby decreasing the intensity of the REP peaks common to both models. The dominant role of the $B(\Pi_3^0)$ state is further confirmed by the partial absorption cross section profiles plotted in Fig. 5.

4. Concluding remarks

The results presented in this paper suggest that the more economic three state model is quite adequate for eliciting the essential features of the IBr photodynamics. The effect of introducing additional states is minimal and easily understood. The unravelling of contributions from individual states to the fundamental Stokes REP $I_{\Pi_3^0}(\omega)$ in this work and also in that of Guo’s calculations, wherein only the $\Pi_3^0$ state was taken to be optically bright indicate that the photodynamics is largely determined by the attributes of the brightest state and that simpler models involving the correct electronic states could be employed advantageously in all photodynamic investigations.

Finally, the basic premise that Raman excitation profiles may be used for model authentication and for obtaining additional insight into the photodynamics seems to be a valid proposition in the light of the results presented here.

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