Experimental and theoretical study of the O+HCI transition state region by photodetachment of OHCI⁻

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We present measured and calculated photodetachment spectra of OHCl⁻, and we interpret the results in terms of the vibrational structure of the transition state of the $O+HCl \rightarrow OH+Cl$ reaction. The measured spectra exhibit two distinct features-an intense broad peak at high electron kinetic energies and a less intense shoulder at lower energies. Superimposed on these broad features are several sharper structures, but they are barely discernible from noise in the spectrum. To interpret these spectra, we have used a recently developed global ${}^{3}A''$ potential surface for the O+HCl reaction to calculate Franck-Condon factors, using an L^2 method (i.e., expansion in terms of square integrable basis functions) to approximate the scattering wave functions on the reactive surface. Assignment of the spectrum has been assisted using the results of quantum coupled channel calculations for the same surface. The resulting calculated spectrum shows the same broad features as the measured spectrum. There is also fine structure with spacings and energies that are similar to the experiment, but specific features do not match. To interpret both the broad and fine features in the theoretical spectrum, a hierarchical analysis is applied wherein this spectrum is decomposed by a tree construction into components of increasingly higher resolution. The physical meaning of each of these components is then determined by plotting "smoothed states" that are obtained from the tree coefficients. This leads to the conclusion that the two broad features in the spectrum are made up of progressions in hindered rotor states of the Cl-OH complex, with the most intense feature corresponding to OH(v=0) and the weaker shoulder corresponding to OH(v=1). There is evidence for Feshbach resonance features in the v = 1 feature, but it appears that most of the fine structure is due to hindered rotor states.

I. INTRODUCTION

The O+HCl \rightarrow OH+Cl reaction is significant both in atmospheric chemistry¹ and as a benchmark for hydrogen atom transfer reaction kinetics.² The reaction is overall nearly thermoneutral, but there is a significant barrier³ (roughly 8.5 kcal/mol) on the ground ³II surface. The reaction has been the subject of numerous theoretical and experimental studies, including reagent state resolved rate measurements,^{4–9} a recent state-to-state measurement of integral cross sections,¹⁰ *ab initio* potential energy calculations,³ trajectory calculations,^{11,12} quantum scattering calculations,^{3,13–15} and transition state theory studies.¹⁶ One interesting feature of this reaction is that quantum scattering studies indicate the possibility of Feshbach resonances associated with the transition state region of the potential surface.^{14,15} Koizumi and Schatz^{14,15} have used a vibrationally adiabatic analysis to calculate resonance positions for scattering on semiempirical London-Eyring-Polanyi-Sato (LEPS) potential surfaces, and the resulting energies are in good correspondence with the position of peaks in the energy-dependent reaction probabilities from scattering calculations. This analysis also indicates that the resonances can be assigned to one of two sets of quantum numbers. In one of these sets, the highest frequency quantum number refers to HCl stretch, while in the other set, the highest frequency quantum number is the OH stretch. This means that some of the resonances are localized mostly in the reagent O+HCl region (and hence have an HCl vibrational quantum number as one of the three labels), and others are mostly in the product Cl+OH region. For v=0 of either HCl or OH, no resonances were found to be stable in the adiabatic analysis (or seen in the scattering calculations), while for v = 1, one resonance for each diatomic was noted, and for v=2, several resonances exist.

Although the theoretical analysis of Koizumi and Schatz . was based on semiempirical potential surfaces and thus may not be correct, it suggests that further work on understanding the transition state structure of the OHCl system might prove fruitful. This suggestion has received further amplification from the work of Zare and co-workers,¹⁰ who found unusual

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structure in the product OH rotational distributions (a sudden dip in the middle of a broad peak) at energies above the HCl(v=2) threshold. Although the energies considered in these experiments are above those considered by Koizumi and Schatz, it seems likely based on the vibrationally adiabatic analysis that resonances should exist under the conditions of the Zare experiment.

In this paper, we present experimental results and theory that are designed to provide further insight into the vibrational structure of the OHCl system. In the experiments, the photodetachment spectrum of the OHCl⁻ ion is measured under conditions where primarily the ${}^{3}\Pi$ surface of OHCl is accessed. Similar photodetachment spectra have been measured in the past for molecules such as CIHC1⁻,^{17(a)} IHI⁻,^{17(a)} FH_2^{-} , $^{17(b),17(c)}$ and OHF^{-} , 18 and in favorable cases, they have yielded significant information about resonances and other types of vibration-rotation energy level structure associated with the transition state region of the neutral species that is produced after photodetachment. The theoretical analysis will use a recently developed ab initio potential surface to study the reaction dynamics and characterize the Franck-Condon factor associated with the photodetachment process. To do this, we use quantum scattering methods to calculate reaction probabilities, and we use L^2 methods to calculate the Franck-Condon factors. We then apply a recently developed hierarchical analysis to interpret structure in the theoretical spectra. With this interpretation, it is possible to make assignments to features in the measured spectrum.

Here is a summary of the rest of the manuscript. In the next section (Sec. II), we describe the experimental measurements and present the measured photodetachment spectrum. The methods and calculations used in the theoretical analysis are presented in Sec. III, while the results of the analysis and the interpretation of the spectra are presented in Sec. IV. Section V summarizes our conclusions. Additional details concerning the hierarchical analysis are provided in the Appendix.

II. EXPERIMENT

The spectrum reported here was recorded on the Berkeley negative ion photoelectron spectrometer. This instrument has been described in detail previously.^{18,19} The OHCl⁻ ion is formed in a pulsed molecular beam by electron impact on a 0.5% mixture of HCl in N₂O. The OH³⁵Cl⁻ ion is selected by time of flight in a Wiley-McLaren type mass spectrometer when crossed by the fifth harmonic of a pulsed Nd:YAG laser (213 nm, 6 mJ/pulse). Care was taken to eliminate the ion $O^{-}(H_2O)_2$, which has the same mass and also tends to be present in the ion beam. A small solid angle of the ejected photoelectrons from OHCl⁻ is collected at the end of a one meter field-free flight tube. The kinetic energy of each detected electron is determined by its time of flight. The polarization of the photodetachment laser is set to be perpendicular to the direction of electron collection. The ion's photoelectron spectrum is signal averaged over several hundred thousand laser shots. The instrumental resolution is approximately 10 meV.

Figure 1 shows the experimental spectrum (along with a theoretical spectrum described in Sec. IV B). The signal rises



FIG. 1. Experimental photodetachment spectrum for OHCl⁻ recorded at 213 nm (5.82 eV). Also shown is the calculated spectrum (dashed line) from the L^2 calculation, using a width parameter of $\sigma=0.155$ eV. The electron kinetic energy $E_{\rm el}$ is related to the OHCl scattering energy E by Eq. (2).

at ~1.6 eV, indicating an electron binding energy for OHCl of ~4.2 eV. There are two prominent features in the recorded spectrum—a broad intense peak centered at 1.3 eV and a less intense plateau at lower electron kinetic energies (corresponding to higher neutral scattering energies). Both appear above the thermodynamic asymptotic energy for formation of ground state O+HCl or OH+Cl and thus the states that give rise to these features are unstable with respect to dissociation. The main peak is ~0.28 eV wide. There is a strong suggestion of substructure on the main peak and indeed also on top of the plateau, but the relatively poor experimental signal to noise precludes confirmation of this point. It is interesting to note that there is considerably less structure in this spectrum in comparison to the photoelectron spectrum of the analogous OHF⁻ system.¹⁸

III. THEORETICAL CALCULATIONS

A. Properties of OHCI⁻ and OHCI

In order to calculate Franck-Condon factors for photodetachment of OHCl⁻, it is necessary to determine its equilibrium geometry and vibrational frequencies. Since these properties have not previously been reported in the literature, we calculated them using Gaussian 90^{20} using a 6-31+++G(d,p) basis and second order unrestricted Møller-Plesset (UMP2) treatment of electron correlation (see Ref. 18 for additional details in an application to OHF⁻). We find that OHCl⁻ has a linear equilibrium geometry (² Π electronic state) with $R(O-H) = 1.889a_0$ (1.00 Å), $R(H-CI) = 3.950a_0$ (2.09 Å), and $R(O-CI)=5.839a_0$ (3.09 Å). The harmonic frequencies are 211 cm⁻¹ for the symmetric stretch-like mode, 3305 cm^{-1} for the antisymmetric stretch-like mode, 635 cm⁻¹ for the bend associated with the A' surface, and 769 cm⁻¹ for the bend for the A" surface. The normal coordinates Q_{ss} , Q_{as} , and Q_{b} (obtained from the harmonic force field analysis in Gaussian) are related to the coordinates R(H-CI) and R(O-H), and the O-H-CI bend angle θ by (atomic units used throughout)

$$\theta(\mathrm{rad}) = \pi - 0.018\ 55Q_b,\tag{1a}$$

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$$R(H-Cl) = 3.950 - 7.079 \times 10^{-3}Q_{ss} + 0.022 \ 58Q_{as},$$
(1b)

$$R(O-H) = 1.889 + 1.643 \times 10^{-4} Q_{ss} - 0.024 \ 05 Q_{as}.$$
 (1c)

Note that the negative ion has a large H-Cl distance, which means that it is best thought of as $Cl^-\cdots HO$. This means that after photodetachment, the OHCl neutral is initially at a geometry which is on the "product" side of the O+HCl reaction barrier. This means that most of the information contained in the spectrum is determined by the Cl+OH collision dynamics. Nonetheless, the photoelectron spectrum does probe the transition state region of the O+HCl surface. Were this not so, the spectrum would simply be that of Cl^- shifted to lower kinetic energy by the $OHCl^-$ dissociation energy.

In order to establish the relationship among the measured quantity, the photoelectron kinetic energy and the neutral OHCl energy of our simulation, the dissociation energy for the OHCl⁻ species must be determined. As no experimental data exist, once again we estimate the quantity from *ab initio* calculations. At the MP2/6-31++G(d,p) level, $D_0^0(OH-Cl^-)=0.735$ eV. If this is combined with the known electron affinity of Cl (3.613 eV), the OH dissociation energy (4.623 eV), the HCl dissociation energy (4.618 eV), the photon energy used in the measurements (5.825 eV), and the OH zero point energy (0.229 eV), one finds that the energy *E* of the neutral OHCl (measured relative to O+HCl with HCl at classical equilibrium) is related to the electron kinetic energy by

$$E_{\rm el} = \Delta E - E, \tag{2}$$

where $\Delta E = 1.701$ eV. In making comparisons with experiment, we will adjust ΔE to give the best fit. However, we find that this optimized ΔE is within 0.076 eV of the *ab initio* estimate, and well within the latter's error bar.

The OHCl potential surface was taken from Koizumi et al.³ This surface describes the ${}^{3}A''$ component of the ${}^{3}\Pi$ state that is produced from the interaction of $O({}^{3}P)$ with HCl. The other component $({}^{3}A')$ coincides with ${}^{3}A''$ for linear geometry, but should be more repulsive for bent OHCl. We have not attempted to include for this in the calculation as we do not have information about the transition moments to enable combining results for the two surfaces. We expect that its contribution to the spectrum will be similar in appearance to ${}^{3}A''$, but shifted to higher *E* by approximately the difference in OHCl bend zero point energy associated with geometries in the Franck–Condon region. This shift is small enough (a few hundredths of an electron volt) that it will not affect broad features in the spectrum, but it could make any fine structure complex.

The ${}^{3}A''$ surface is an analytical fit to extensive *ab initio* calculations. Its barrier was adjusted to give thermal rate constants at 300 K which match experiment. The resulting barrier energy is 8.50 kcal/mol, and it is located at $R(O-H)=2.33a_0$ (1.23 Å), $R(H-CI)=2.62a_0$ (1.39 Å), and $\theta=133.4^{\circ}$. There is also a linear geometry saddle point, located at $R(O-H)=2.10a_0$ (1.11 Å) and $R(H-CI)=2.50a_0$ (1.32 Å), and having an energy $V_b=10.39$ kcal/mol.

B. Quantum scattering calculations

Reaction probabilities for the O+HCl reaction have been calculated using a hyperspherical coordinate-based coupled-channel method, the details of which are given elsewhere.²¹ Only the J=0 partial wave was considered. Numerical parameters used in the calculations are similar to what has been described previously¹⁵ for applications with LEPS surfaces. In the present calculations, we used a basis set of four vibrational functions for both the O+HCl and Cl+OH arrangement channels, with 20 rotational states (j=0-19) for each vibrational function. This makes the total number of states be 80 for each arrangement channel, or 160 total.

In the present application, only the cumulative reaction probability $P_{\text{cum}}(E)$ and its vibrationally resolved counterpart $P_{vv'}(E)$ need to be considered. These are defined in terms of the state-to-state reaction probability P(vj,v'j';E)using

$$P_{\rm cum}(E) = \sum_{vj} \sum_{v'j'} P(vj,v'j';E),$$
 (3a)

$$P_{vv'}(E) = \sum_{j} \sum_{j'} P(vj, v'j'; E).$$
 (3b)

Note that we do not include the electronic angular momentum in our description of OH, and as a result, only the OH rotational angular momentum j' is included.

C. *L*² calculations of photodetachment Franck–Condon factors

It is possible to use coupled-channel calculations to determine scattering wave functions for the purpose of calculating Franck-Condon overlaps with the negative ion initial state,²² however, we found that this calculation was ill behaved for OHCl⁻, presumably because of numerical problems with unfolding the stabilizing transformations that are used during the propagation. To circumvent this problem, we have used an L^2 method originally proposed by Bowman and co-workers,²³ in which the Hamiltonian of neutral OHCl is diagonalized in a basis of square integrable basis functions which covers the OHCl transition state region. The wave functions thus obtained are only approximations to the true OHCl continuum states, but within a certain time scale, they are realistic [i.e., time scales too short to reach the unphysical boundaries imposed by the L^2 calculation (see the results in Sec. IV B, particularly Fig. 9]. Overlaps of these wave functions with the corresponding OHCl⁻ states determine the desired Franck-Condon factors. The spectrum in this case comes out in the form of a "stick" spectrum, but it is customary to convolute this with a Gaussian whose width is determined by the experimental resolution in making comparisons with experiment. In this paper, we will extend this convolution procedure to perform a hierarchical analysis of spectra as described in the next section.

The L^2 calculations have been done using a discrete variational representation (DVR) approach²⁴ to express the Hamiltonian matrix, coupled with a sequential diagonalization-truncation (SDT) method^{23,24} to find its eigenvalues. Since our implementation has not been presented previously, we give details of the calculations here. Since the negative ion wave function is localized in the product region, the Hamiltonian is written using Jacobi coordinates R, r, and γ associated with the Cl+OH arrangement of the atoms, where R is the scaled distance between the center of mass of OH and Cl, r is the scaled OH internuclear distance, γ is the angle between the vectors along R and r, and μ is the scaled reduced mass. For J=0, we find (using atomic units)

$$H = -\frac{1}{2\mu} \left(\frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{1}{r} \frac{\partial^2}{\partial r^2} r \right) - \left(\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2} \right)$$
$$\times \frac{1}{\sin \gamma} \left(\frac{\partial}{\partial \gamma} \sin \gamma \frac{\partial}{\partial \gamma} \right) + U(r, R, \gamma). \tag{5}$$

In the SDT method, we first solve one dimensional eigenvalue problems associated with the coordinate r, with the other coordinates treated as parameters. The Hamiltonian for this one dimensional problem is

$$H_1(r;R,\gamma) = -\frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + U(r;R,\gamma)$$
(6)

and the basis used is the Fourier sine series

$$\langle q_n | r_i \rangle = \sqrt{\frac{2}{N_r}} \sin q_n (r_i - r_{\min}),$$
 (7)

where

$$q_n = \pi n / L_r, \quad n = 1, \dots, N_r, \tag{8a}$$

$$r_i = r_{\min} + L_r i/N_r, \quad i = 1, \dots, N_r,$$
 (8b)

$$L_r = r_{\max} - r_{\min}. \tag{8c}$$

The parameters r_{\min} and r_{\max} are the minimum and maximum values of the *r* coordinate where the wave function was chosen to be zero. After diagonalizing H_1 , we obtain the eigenvalues $E_{1,n}(R,\gamma)$ and the amplitude of the eigenfunctions $f_{1,n}$ at the discrete points r_i $(i=1,...,N_r)$. We only use the eigenvalues and eigenfunctions below a cut-off energy $E_{\max 1}$.

Next we solve the two dimensional problem associated with the coordinates r and γ . The two dimensional Hamiltonian is

$$H_{2} = -\frac{1}{2\mu} \frac{\partial^{2}}{\partial r^{2}} - \left(\frac{1}{2\mu R^{2}} + \frac{1}{2\mu r^{2}}\right) \frac{1}{\sin\gamma} \left(\frac{\partial}{\partial\gamma} \sin\gamma \frac{\partial}{\partial\gamma}\right) + U(r,\gamma;R).$$
(9)

Here we use a basis set which consists of products of the eigenfunctions $f_{1,n}$ for the r coordinate and Legendre polynomials P_j for γ ,

$$\langle r_i, j | n, \gamma_{\alpha} \rangle = f_{1,n}(r_i; R, \gamma_{\alpha}) \sqrt{\frac{(2j+1)\omega_{\alpha}}{2}} P_j(\cos \gamma_{\alpha}),$$
(10)

where γ_{α} and ω_{α} are the roots and weights for Gauss-Legendre quadrature. The eigenvalues obtained by diagonalizing H_2 using this basis set are called $E_{2,n}(R)$ and the eigenfunctions are called $f_{2,n}$. These states are truncated by a cut-off energy $E_{\max 2}$. Finally we solve the three dimensional problem. In this case, the basis sets combine the eigenfunctions $f_{2,n}$ for r and γ with a Fourier sine basis for R,

$$\langle r_k, Q_i, j | n, R_j \rangle = \frac{1}{r_k R_j} f_{2,n}(r_k, \gamma_\alpha; R_j) \sqrt{\frac{2}{N_R}} \\ \times \sin Q_i(R_j - R_{\min}), \qquad (11)$$

where

$$Q_k = \pi k / L_R, \quad k = 1, \dots, N_R,$$
 (12a)

$$R_j = R_{\min} + L_R j / N_R, \quad j = 1, \dots, N_R,$$
 (12b)

$$L_R = R_{\max} - R_{\min}. \tag{12c}$$

After diagonalizing the full Hamiltonian H, eigenvalues E_k and eigenfunctions χ_k needed for the photodetachment calculation may be obtained.

Our SDT calculations for the OHCl system used an r interval between 1 and $5a_0$, and an R interval between 3.5 and $8.0a_0$. The grid consisted of 32 points for r and γ and 28 for R. The upper limit energies were taken to be 0.04 hartrees for both r and r, γ parts of the calculation.

Photodetachment spectra are calculated using the Franck–Condon factor for transition from the negative ion initial state and the neutral species final state. A discussion of the approximations associated with use of this Franck–Condon factor have been given elsewhere by Schatz.²² The Franck–Condon factor F(E) is defined using the formula

$$F(E) = |\langle \phi | \chi(E) \rangle|^2, \tag{13}$$

where ϕ is the initial vibrational state, χ is the final vibrational state, and *E* is the energy associated with the state χ . If χ were a true continuum final state, *F* would depend on the asymptotic state labels associated with that state, and we would have to sum *F* over these states to define the measured intensity. However, when χ is approximated by L^2 functions, there is only one state at each energy, and no sum is needed. Implicit in our expression for *F* is an integration over the Euler angles which locate the plane of the OHCl triatomic. Here we use only the J=0 rotational states for ϕ and χ . Other states may contribute to the experiment, but the large moment of inertia associated with OHCl makes rotational broadening small.

D. Hierarchical analysis of spectra

The Franck–Condon factor F(E) defined in the previous section is only obtained at discrete energies when L^2 functions are used to approximate the continuum eigenfunctions. Following earlier work by Gazdy and Bowman,²³ it is possible to define a "smoothed" spectrum S(E) by convoluting F(E) with a Gaussian function G, i.e.,

$$S(E) = \int F(\epsilon)G(E-\epsilon)d\epsilon, \qquad (14)$$

where

$$G(E) = \exp(-E^2/\sigma^2).$$
⁽¹⁵⁾

In past work, the width parameter σ in G has been chosen to either match the experimental width, or to make theory and

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experiment look as much alike as possible. However, it is possible to learn much more about both the spectrum and the wave functions which underlie it by letting the width be a variable parameter and studying how the results vary with σ .

Several recent papers²⁵⁻²⁸ have described a systematic procedure to study a spectrum as resolution is changed in a continuous manner. Previous applications have been for bound to bound spectra²⁵⁻²⁹ and have involved two related types of analyses. First, for either experimental or theoretical spectra, one can generate a hierarchical decomposition of a spectrum. This involves the generation of a hierarchical tree (see Sec. IV C). The tree can be analyzed using techniques developed in the classification and multivariate analysis literature (see, e.g., Refs. 30 and 31). The analysis can be grouped into three types; (1) dimensionality; (2) clustering; and (3) number of time scales implied by a spectrum. All these measures give information concerning pathways and time scales for intramolecular energy transfer (see particularly Refs. 27, 28, and 29). They can also be employed as a tool for assigning features of smoothed spectra by indicating at what level of smoothing a particular spectrum is "interesting."

When a theoretical version of a spectrum generated from the eigenstates of a particular system is available, one can generate very specific information concerning energy transfer and assignability. This involves the generation of smoothed states from the grouping of eigenstates indicated by a hierarchical tree representation of the spectrum. A hierarchical tree is a nested set of subsets, and in the case of a spectrum, each subset is a grouping of eigenstates. Each of the groups can be summed in the following manner:

$$\Phi(R,r,\gamma) = \sum_{j} c_{j}\chi_{j}(R,r,\gamma), \quad j \in L,$$
(16)

where L refers to the Lth group and j to the jth element of group L. The c_j 's in Eq. (16) are merely the amplitudes, the overlap of the initial state with the eigenstate, or the square root of the intensity [see Eq. (13)]. The state Φ generated in this manner is associated with a given feature of a smoothed spectrum. By studying series of smoothed states generated at a given level of resolution, one can address issues of assignability, and by following specific paths down the tree, one can study energy transfer pathways. Explicit examples of these are presented in Refs. 27 and 28 and Sec. IV D.

IV. RESULTS OF THEORETICAL CALCULATIONS AND ANALYSIS

A. Quantum reaction probabilities

Figure 2 presents the cumulative reaction probabilities $P_{\rm cum}(E)$ and $P_{vv'}(E)$ as a function of the energy E for (vv')=(00), (01), (10), and (11). The results in this plot are similar to what has been presented previously for the Persky-Broida #1 (PB1) surface.¹⁵ Note that the energetic threshold for the ground state reaction is at 0.22 eV, while that for O+HCl(v=1) is at 0.54 eV and that for Cl+OH(v'=1) is at 0.66 eV.

The adiabatic barrier for O+HCl is at 0.47 eV (using harmonic zero point energies), so one does not expect sig-



FIG. 2. Cumulative reaction probability vs OHCl energy E (the internal energy of the OHCl in electron volts) for O+HCl using the fitted *ab initio* surface. Included in the plot are both the total cumulative probability $P_{\text{cum}}(E)$ (solid line) and the vibrationally state resolved probabilities $P_{nn'}(E)$ with vv'=(00), (10), (01), and (11). The line types used for these curves are chain dash (00), dotted (11), dashed (10), and chain dot (01).

nificant reactivity at energies much below that in Fig. 2. Indeed it is clear from Fig. 2 that P_{cum} is relatively small at energies significantly below this, however, in contrast to what is seen for LEPS surfaces, one finds in Fig. 2 that P_{cum} rises up only gradually near the reaction threshold, not achieving a value of unity until E=0.69 eV. In addition, notice that $P_{\rm cum}$ shows smooth steps at low energies, with a spacing of roughly 0.06 eV. This spacing corresponds reasonably well with the symmetric stretch quantum at the saddle point, suggesting that the steps are due to reaction through a progression of adiabatic energy levels of the transition state. This by itself is not especially surprising,³² but the surprise is that the cumulative reaction probability increases by much less than unity with the appearance of each new step. A unit increase would mean that 100% of the flux that crosses the reactive bottleneck proceeds to products. An increase of less than unity indicates that flux is getting reflected back to the reagents. This often happens because of reaction path curvature (the "bobsled effect"). In the present case, it appears that curvature effects are much more significant for the fitted ab initio surface than for the earlier LEPS surfaces. This result is consistent with the fact that the fitted surface has a nonlinear geometry saddle point (so there is curvature in both bend and stretch motions), while the LEPS surface saddle point is linear.

Perhaps the most noticeable features of the curves in Fig. 2 are sharp peaks which occur at 0.693 and 0.77 eV. Somewhat less distinct peaks are found at 0.84, 0.905, 0.95, and 0.99 eV. Based on our work with LEPS surfaces, it is possible to assign some of these peaks as due to trapped state resonances. For example, the first two peaks are also seen in the LEPS results, where a diagonally corrected vibrationally adiabatic (DIVAH) analysis indicates that they may be labeled HCl(1)₀₀ and OH(1)₀₀, respectively. The notation HCl(1)₀₀ means that the resonance state correlates adiabatically with the HCl(v=1) vibrational state, and that the O-HCl stretch quantum number and bend quantum number are both zero. OH(1)₀₀ similarly refers to a state that correlates adiabatically with OH(v=1). The higher energy reso-

nances presumably involve excited state bends and stretches, but we have not attempted to assign them as there are several possible choices of quantum numbers. Note, however, that for the LEPS surface, the DIVAH analysis indicates that $HCl(2)_{00}$ should be located at roughly 0.95 eV, which corresponds with one of the peaks we see. In addition, the DIVAH analysis suggests that only the ground states of the Cl–OH and O–HCl stretch quantum numbers are expected to give narrow resonances, but excited bends are possible. In fact, the bend spacing should be roughly 0.06 eV, which is close to the energy difference between several of the peaks we find.

B. Photodetachment spectra from L^2 calculations

In our discussion of the calculated photodetachment spectra, we will begin by considering low resolution spectra that are obtained using large values of the width parameter σ in the Gaussian weight function G (described in Sec. III), and then we will consider the higher resolution spectra that are obtained with smaller σ values. Figure 1 shows the comparison of calculated and measured spectra for our largest choice of σ (σ =0.155 eV), the one which results in the best fit between the experimental and theoretical spectra. This value of σ is much larger than the experimental width, so it washes out the fine structure in the calculated spectrum. However, this allows us to see how well theory describes the broadest features in the spectrum (a comparison which has often been made in the past²²). In the calculated spectrum, only two significant features are observed, a broad peak near 1.3 eV, and a broad shoulder in the 0.5-1.0 eV range. The correspondence with experiment is excellent at this level of comparison, with both the width and intensities of these two broad features being correctly described. As mentioned in Sec. III A, the energy scale of the calculated spectrum has been adjusted to maximize agreement with experiment. However, this energy conversion (1.625 eV-E) agrees well with our independent estimates. What this also means is that the neutral energy E that corresponds to the peak at 1.3 eV is E=0.4 eV. This energy is in the reactive threshold region of Fig. 2, so apparently the most intense peak in the spectrum is concerned with energies comparable to the top of the barrier to reaction. This type of behavior has been observed in the lowest E part of the ClHCl⁻ photodetachment spectrum, and its physical explanation has been discussed.²² The shoulder region of the spectrum in Fig. 1 corresponds to E=0.7-1.2eV, which includes the resonances seen in Fig. 2. However, it will require additional analysis (see below) to say if resonances contribute significantly to the shoulder.

Figure 3 presents higher resolution portions of the calculated photodetachment spectrum. Note that in Fig. 3, we have switched to the energy E, as all of our remaining analysis concerns theoretical results for which E is the natural energy to use. Figure 3 is broken into four parts, each corresponding to a different width, as determined by the hierarchical analysis of the next two sections. Figure 3(a) shows a slightly higher resolution version of the spectrum of Fig. 1, with σ =0.11 eV. Figure 3(b) shows the spectrum at a still higher resolution (σ =0.011 eV, which is similar to the experimental resolution) and Figs. 3(c) and 3(d) show ex-



FIG. 3. A series of smoothed spectra for the theoretical photodetachment spectrum plotted in the internal energy E. The level of smoothing was chosen from the hierarchical trees of Fig. 4. The σ value used in each plot [see Eq. (15)] is generated for a width which lies halfway between the nodes of the trees of Fig. 4 (halfway between the *n* peaks of each panel in this figure and n+1 peaks). (a) is smoothed with $\sigma=0.11$; (b) is smoothed with $\sigma=0.013$; and (d) is smoothed with $\sigma=0.0096$ (all in electron volts). (a) and (b) show the complete spectrum and (c) and (d) show only portions of the spectrum, with (c) showing the peak in Fig. 1 and (d) showing the 0.5-1.0 eV shoulder of Fig. 1.

panded versions of the two large peaks of Fig. 3(b). The resolution of these latter two smoothed spectra were generated from window functions whose widths are 0.013 and 0.0096 eV. (The small differences between these values is not important to the present discussion, but will be useful in Sec. IV D.) Figures 3(b)-3(d) indicate that there is substructure in the broad peaks presented in Figs. 1 and 3(a), consisting of rather regularly spaced peaks. We will show below that these peaks are part of a rotor sequence, with the peak spacings corresponding very well to an OH rotor sequence. The states corresponding to the peaks will be assigned in Sec. IV D.

The fine structure in Fig. 3(c) is in many respects similar to the apparent fine structure in the experimental spectrum (Fig. 1), but unfortunately there is sufficient uncertainty about noise in the experiment, and about how to compare theory and experiment, that makes it impossible to come to a firm conclusion concerning the assignment of specific features. One important difference between theory and experiment is in the spacings of the peaks. The four peaks in Fig. 1 located on top of the broad feature at 1.3 eV (electron energy) are spaced by 0.05 eV, while the corresponding first four peaks in Fig. 3(c) (near E=0.3 eV) have a spacing which increases with energy from 0.025 to 0.034 eV. Larger spacings are found in Fig. 3(c) at still higher energy, but there really is not a one-to-one correspondence with Fig. 1. Two possible reasons for this lack of detailed correspondence are errors in the ${}^{3}A''$ surface (which was not optimized in the Franck–Condon region) and contributions from the ${}^{3}A'$ surface that were not included (as discussed in Sec. III A).

C. Hierarchical analysis of spectra

In the previous subsection, smoothed versions of the OHCl⁻ stick spectrum were presented in Fig. 3 and they indicated that the dominant features in the spectrum were two peaks which are denoted v=0 (at E=0.4 eV) and v=1 (0.7-1.2 eV) because they refer to a short vibrational progression in a motion which is mostly OH stretch (see Sec. IV D also). In addition, these peaks exhibit fine structure with higher resolution. The level of smoothing used to generate these pictures was discerned from a hierarchical analysis of the theoretical stick spectrum and some of this analysis is described here.

The original motivation for developing the hierarchical analysis revolved around the fact that although spectra of highly excited molecules could be very complicated, smoothed versions of the spectra can show distinct "clumping" (see, e.g., Ref. 33 and the references cited there and in Refs. 26 and 27). In the past, the smoothing had generally not been done systematically and had only been done for a few levels of resolution. The hierarchical analysis is meant to address these two drawbacks by systematically viewing the spectrum as resolution is changed in a continuous way and by examining the spectrum at all levels of resolution. In addition, one can use several analysis tools to discern what levels of resolution are important over a whole spectrum or over portions of the spectrum. Also, as shown in the next subsection, when the eigenstates of the systems are available, one can generate states associated with smoothed spectral features that can be used to assign the features and to study energy transfer properties.

By using the smoothing function shown in Eq. (15) and varying σ in a continuous fashion (i.e., over very small steps), one can monitor the way a spectrum changes with resolution. In particular, it is possible to characterize the splitting of peaks as resolution is increased, and by keeping track of this splitting process as a function of σ , a genealogy of peaks can be developed. A convenient way to visualize the relationships between all these peaks is to plot the widths at which peaks appear and from what peaks they branch, generating a hierarchical tree. Such a tree has been developed for the spectrum obtained from the L^2 eigenstates, and the results are plotted in Fig. 4. The top tree in Fig. 4 shows the branching pattern for the v=0 peak and the bottom tree for the v=1 peak. Once again, these plots and all subsequent plots are generated for the spectrum represented in the internal energy of the OHCl complex. The numbers given at the bottom of each tree indicate the line numbers from the stick spectrum (in order by energy) used in constructing the tree. [Hierarchical trees such as the ones presented here should be thought of as mobiles. That is, all their properties remain



FIG. 4. The top tree is for the peak of Fig. 3(c) and the bottom tree is for the peak of Fig. 3(d). The label "width" refers to σ . The horizontal dotted line drawn on the top tree is used to make a cut across the tree to generate subtrees in Fig. 5. The precise vertical location of the dotted line is not important in generating the subtrees, merely that it lies between the eighth highest node at 15 meV and the ninth highest node at 10 meV.

unchanged when the tree is rotated around any node. Therefore the abscissas of the trees do not have meaning in the usual sense, with the only meaningful quantities along the horizontal being the labels at the bottom of each terminating branch of the tree, which here refer to lines of a spectrum. However, to make a visual connection with the spectrum, the terminating branches of the trees are adjusted to match the spectrum, but it is improper to think of an (x,y) pair of points as having any meaning. Further details are provided in Ref. 26.]

Two important properties of hierarchical trees such as the ones plotted in Fig. 4 are the nature of the branching and the values of the widths where splittings (nodes) occur. With this information, one can define relationships among all the lines of the spectrum. For example, we can define the "distance" between two lines as the width associated with their most recent common ancestor. Thus in the top tree, the first and last lines meet at the top of the tree at a width of 23.5 meV, and the first and second lines meet at a width of 2.5 meV. Note that the first and third lines also have the same most recent common ancestor, and the distance between



FIG. 5. A set of subtrees cut from the top tree of Fig. 4 using the dotted line drawn there. The solid dots plotted on (d) show a path down the tree which will be studied in Sec. IV D.

them is also 2.5 meV. (The first three lines noted here are in the lower left of the v=0 tree in Fig. 4 above the number "9.") The matrix of distances between all the lines can be used to perform a statistical analysis of spectra,²⁶ which is useful for identifying important spectral features. This analysis was used to supplement what is presented here.

It is straightforward to read from the trees of Fig. 4 the number of peaks present for a given width. This is merely the number of vertical lines which are crossed by a horizontal line drawn across the tree at that width. For example, there are nine lines in the v=0 peak at a width of 12 meV. This corresponds to a time on the order of 30 fs after the initial formation of OHCl. Note that between the widths 9 and 15 meV, the number of lines in the v=0 spectrum is almost constant (one line is added at 10 meV). We use the term "gap" to denote such a distinct range of widths such as this which is devoid of nodes. A similar gap exists in the v=1peak, but only over a limited spectral range in the middle of the tree. When this sort of gap occurs, it means that there is some sort of time scale separation between different types of motion in OHCl. In order to determine what kinds of motion are involved, it is necessary to examine states which correspond to portions of the trees in Fig. 4 that are above and below the gaps. This is considered in the next subsection.

Let us now consider the "subtrees" that are generated by cutting across the v=0 tree at a width between 10 and 15 meV (see the dotted line on Fig. 4), corresponding to the gap region just discussed. Figure 5 shows four of these subtrees, with the labels (a)-(d) in this plot corresponding to the features labeled 1-4, respectively, in Fig. 3(c). The line numbers associated with each of these subtrees are given at the bottom of each subtree.

We will show in the next subsection that the subtrees in Fig. 5 are related to each other in that they correspond to a progression in hindered rotor states of the Cl-OH complex. This suggests that the subtrees might be similar in appearance, but what Fig. 5 reveals is that the structure within each subtree varies from one subtree to the next, with only a few



FIG. 6. Two states which correspond to the two peaks of Fig. 3(a). The coordinate system is defined in the text with R=5.91 a.u. These plots show the short H-stretch progression. The dotted lines show potential contours from 0.5 to 2.5 eV at 0.5 eV increments. The real number at the top of each plot indicates the maximum of each wave function and the pair of integers the range of eigenstates summed to form the wave function, which is plotted as $|\Phi|^2$. There are five contour heights which are chosen based on the algorithm $j \times (\max/6)$, with j running from 1 to 5.

persistent features. One common feature of the four subtrees is that they all have a distinct splitting into two groups, as evidenced by the gaps between the first and second nodes at the tops of the trees. Note that this splitting structure does not extend to the low energy subtrees in Fig. 5. This is what would be expected for a rotor state progression, where the low J states have very different time scales than the high Jstates.

There are some additional discernible groupings in the subtrees in Fig. 5. These are indicated by gaps between widths of 0.4 and 3 meV, and are indicative of progressions in states associated with Cl–OH relative translational motion (see Fig. 12 in the next subsection and Fig. 14 in the Appendix). This is as one would expect, namely that the translational time scale should be the slowest one in the spectrum.

In summary, in this subsection we have used a tree analysis to systematically study the structure in the OHCl photodetachment spectrum. This analysis indicates there is



FIG. 7. These smoothed states correspond to the peaks of Fig. 3(c) with the numbers (1-4) on that plot referring to the states from top to bottom in this current figure. These are a set of hindered rotor states with J increasing (seven for the top state and ten for the bottom). Once again, R=5.91 a.u. The integer numbers on each plot once again refer to the range of spectral lines used to generate the states, as well as the maximum of each $|\Phi|^2$.

one strong time scale separation in the spectrum and then additional, but less distinct structure at higher resolution. Although it is sometimes possible to make spectral assignments based on peak spacings alone, we will not attempt this here as the smoothed states which we now consider enable a more definitive assignment.

D. Smoothed states

Using Eq. (16) and the analysis of the previous subsection and Ref. 26, it is rather straightforward to examine a smoothed spectrum for the assignment of its peaks and to study energy transfer pathways. Figure 6 shows two plots which correspond to the lowest resolution spectrum, presented in Fig. 3(a), and Fig. 7 shows a series of four plots which correspond to the peaks in Fig. 3(c). These plots are presented in the Jacobi coordinates described above, with R fixed at 5.9107 a.u., one of the values used in the DVR calculation of Sec. III C. In these plots, the OH center of



FIG. 8. A series of smoothed states at various values of R (labeled on each plot, in atomic units) for the state on the bottom of Fig. 7. These plots once again show the maximum value of $|\Phi|^2$.

mass is at the origin and the Cl atom is fixed along the x axis (i.e., y=0 corresponds to linear ClOH). The coordinates of the H atom relative to the OH center of mass are the (x,y)values. One can observe in Fig. 6 that the two peaks represent v=0 and 1 of a short H-stretch progression, with the stretch mostly being OH in character. Figure 7 further demonstrates that the extra structure on top of the v=0 peak of Fig. 3(c) is a series of hindered rotor states, with the four states of Fig. 7 spanning the values J=7-10. Actually the spacings of the peaks are in excellent correspondence with a simple OH rigid rotor energy expression, suggesting that the states are close to free-rotor character. However, we show in the next two paragraphs that the rotor states are better thought of as hindered rotor rather than free.

The states shown in Figs. 6 and 7 are a single slice at fixed value of R, but we have enough information to study the states in many different ways. First, Fig. 8 shows the J=10 state at several different values of R taken from the DVR grid. One can observe that the character of the state is not cleanly a single rotor (it may be difficult to count the number of nodes). Figure 9 once again shows the J=10 state, but now at a fixed value of r, with variation in R and γ . The value of the OH bond distance is fixed at its equilibrium value of 1.833 a.u., although almost any reasonable value would work since there are no nodes along the r direction in the plots of Figs. 7 and 8, this being the v=0 channel. The plots in Figs. 7 and 8 also demonstrate why we refer to the states as hindered rotors, since those states which show a

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FIG. 9. Another representation of the state of Fig. 8. This is a plot in R and γ , with the OH bond distance fixed at its equilibrium value (1.833 a.u.). The solid contours are positive values of Φ and the dotted lines are negative values.



FIG. 10. A series of plots of states associated with the 14 peaks of Fig. 3(d). Once again, the maximum of each $|\Phi|^2$ is shown as well as the range of eigenstates summed to form the smoothed states. Note that the last 12 plots are a progression in hindered rotor states, as were those of Fig. 7, but now there is at least one radial node because these are above the threshold for v=1. Note also that there is considerable mixing between the v=0 and v=1 channels. The first state (upper left) is actually still part of the v=0 progression and the second state (middle top) has the appearance of a bend state for reasons discussed in the text. The last two states show evidence of v=2.



FIG. 11. A series of states from the path indicated by the dots on Fig. 5(d), except for the first state, which is associated with the v=0 peak. The headings have the same meaning as previous plots of this type (e.g., Fig. 10). Note that there is evidence of reaction in the last plot, although the wave function has a low density. See the text for further details.

complete set of nodes are pinched in as the H atom moves between O and Cl at y=0.0 (collinear).

The representation of the wave function in Fig. 9 makes several interesting points. First, it demonstrates again that this is mostly a J=10 state, and once again shows that the state is not a perfect rotor. The density buildup is such that it explains why many of the R slices in Fig. 8 are incomplete. The buildup shows considerable distortion from a pure rotor state and this causes the variation in intensity of the slices in Fig. 8. One of the most important aspects of Fig. 9 is that density is well away from the edges of the box used to generate the stick spectrum, which are at 3.5 and 8.0 a.u. This demonstrates fairly conclusively that the structure observed in the spectra of Figs. 3(a)-3(d) is realistic, at least for the potential surface used. A similar analysis of the v=1 hindered rotor states presented in Fig. 10 (plotted in the same x, y coordinate system as Fig. 6) also demonstrates that the structure in these spectra is physical.

The set of hindered rotor states presented in Fig. 10 is considerably more complicated than those of Figs. 7-9, since both the v=0 and 1 channels are open for most of the states, and v = 2 is manifested in the last two. The first state in the upper left is still part of the v=0 progression, but many higher resolution states demonstrate v=1 character in this energy range. Although it may not be apparent from this particular slice, the first state has J=13, which is the next rotor state in the progression from the first peak. It should be noted that at higher levels of resolution, one can observe still higher J values of the v=0 hindered rotor states at higher energy. The states after the first two in Fig. 10 once again are a progression in hindered rotor states, but with v = 1 in the OH stretch. The second state plotted (labeled 464-521) appears to be more of a bend state, and has this type of character because it is a superposition of the rotor states ranging from J=0-3 (this particular time scale is not sufficient to resolve the longer period low J rotor states). It is also noteworthy that this 464-521 state coincides in energy with the first resonance in Fig. 2, as this may contribute to the some-

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FIG. 12. Jacobi coordinate plots (see Fig. 9) of the same states as Fig. 11.



FIG. 13. The time development of the wave packet formed from the photodetachment is presented here (the plots show the real part of the wave packet). This wave packet was formed from the superposition of the eigenstates of the L^2 calculation. The coordinate system is the same as that of Fig. 9. The headings show both the maxima and the time at which the wave packet is presented.

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FIG. 14. A series of plots of the eigenstates of the L^2 calculation. These show a complete set of eigenstates used to generate the smoothed state in the lower left of Fig. 12, with the exception of the 296th state which has a very low coefficient. Note that the coefficients are listed above each plot, but are scaled relative to the 293rd state, which has the highest value for this range. The coefficients are listed on the second line from the top above each of the plots. Both the maximum of each Φ and the state number are shown on each panel. The coordinate system is the same as Fig. 9.

what larger intensity of the peak associated with it. Similarly, the 615–658 peak coincides with the second resonance in Fig. 2, and is also enhanced in intensity.

The plots up to this point (Figs. 6-10) have addressed the issue of assignability as discussed above. We now present results concerning energy transfer by following a pathway down the tree. This energy transfer is important to the OH vibration/rotational distributions that are produced when the Cl-OH complex dissociates, and it also causes rearrangement of the Cl-OH complex to form O-HCl and then O+HCl. Figure 11 shows a set of plots in the (x,y) coordinate system of Fig. 6. These follow a specific pathway down

the tree on the top of Fig. 4. The last five plots in the figure are indicated on the subtree of Fig. 5(d) as five large dots. The first plot corresponds to the top node of the tree at the top of Fig. 4. The first two plots have been previously presented in Figs. 6 and 7, respectively.

The first two panels of Fig. 11 demonstrate explicitly the way in which the OHCl complex moves. These plots are generic for most of the structure evident in Figs. 3(c) and 3(d). What first occurs after formation of the neutral is H-atom stretching, which is mostly OH in character. Then the H atom starts moving in what either looks like a bend for small values of O-Cl or hindered rotation for larger values of O-Cl, as is shown in Fig. 11. The bend/hindered rotor motion is always centered on the OH side of the complex. This energy transfer process is not surprising based on the different time scales for the motion, the nature of the potential energy surface, and previous work on the photodetachment spectra of heavy-light-heavy systems.²²

The next three panels of Fig. 11 look essentially the same as the second with OH hindered rotation. However, R/γ slices of the same wave functions are presented in Fig. 12 and these indicate what type of motion the complex is undergoing. Panels 3-5 of Fig. 12 show that the complex is moving out to larger values of R, the O–Cl distance. In fact, the fifth panel takes the wave function to the upper limit of the DVR grid (8.0 a.u.). At the same time, some of the wave function is moving to larger O-Cl distances; these three panels of Fig. 11 demonstrate that the H atom remains affixed to the O atom. However, this pathway down the tree includes the formation of HCl as indicated by the final panel of Fig. 11, where some of the density now lies on the HCl side. Note, however, that the maximum of the plot lies at 1.68×10^{-8} , which is considerably smaller than the previous three plots which are on the order of 10^{-6} , indicating that this is a small probability event. Note also that this final panel is at the edge of applicability because the fifth panel of Fig. 12 shows a wave function at the edge of the grid and the sixth panel of Fig. 12 shows interference structure which is almost certainly related to reaching the edge of the grid.

In this subsection, we have presented results based on the analysis of smoothed states. There are alternatives to this approach, including the study of wave packet dynamics and the direct analysis of the eigenstates from the L^2 calculation. The Appendix has a brief discussion of these two as compared to the analysis presented in this subsection.

V. SUMMARY OF CONCLUSIONS

This paper has presented a broad-ranging study of the photodetachment spectroscopy of OHCl⁻ that started with the measured spectra and proceeded through a series of theoretical studies based on scattering calculations and on wave functions and spectra that are derived from L^2 calculations. The spectra show two broad features that correspond well with theory based on the ³A" surface of Koizumi *et al.* The interpretation of these features based on the analysis of smoothed states is that they correspond to the production of Cl-OH(v=0) and Cl-OH(v=1). This result is similar to the interpretation of spectra associated with the OHF⁻ complex, ¹⁸ although in the latter case, more vibrational states

of HF are energetically accessible and have large Franck-Condon factors, so more peaks are observed.

There is apparently fine structure in the measured OHCl⁻ spectra, although resolution problems make it difficult to interpret in detail. The L^2 calculations show fine structure that is qualitatively similar to what is seen in the measurements, but there are quantitative differences in peak spacings that have prevented a detailed assignment of the experimental spectrum. However, we have used a hierarchical analysis of the theoretical spectra, along with smooth states to assign all features in the theoretical spectra. The dominant physical mechanism responsible for this fine structure is hindered rotation of the nascent Cl-OH species. For the v = 0 state of OH, rotational states with quantum numbers ranging from J=4 to 12 are clearly resolvable. For OH(v =1), J=3-12 can be discerned, but other types of states also contribute, including higher J's associated with OH(v=0), and Feshbach resonances. The resonances in this case appear only to modulate the intensity of the rotational progression, which is a much less dramatic effect than has been seen for species like IHI-. However, this result is consistent with the fact that the initial geometry produced in photodetachment of OHCl⁻ is well removed from the saddle point. The hindered rotor progressions that we find are similar to results obtained in previous observations for FH_2^- , $^{17(b)}$ and with earlier theoretical work on ClHCl⁻ and IHI⁻, 22,34

This paper has also demonstrated the usefulness of the hierarchical analysis for assigning spectra and of smoothed states for interpreting spectra. Figure 14 in the Appendix shows that the individual eigenstates obtained from the L^2 calculations are difficult to interpret, while the superposition of these eigenstates used in defining the smoothed state in the lower left of Fig. 12 is relatively straightforward to understand. An alternative to the present analysis would have been to use wave packets, as is demonstrated by Fig. 13 in the Appendix. However, the wave packet gives nonspecific information, whereas the tree diagrams in Fig. 4 and the smoothed states in Fig. 12 provide a systematic and informative decomposition of the same data that is more directly coupled with the spectra.

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APPENDIX: WAVE PACKETS, *L*² EIGENSTATES, AND SMOOTHED STATES

The hierarchical analysis of Sec. IV C provides a means to systematically "divide and conquer" a molecular spectrum. That is, it provides a systematic means to view a spectrum on all levels of resolution in both time and energy, so that one way of thinking about the smoothed states of Sec. IV D is that they result from a calculation which is a hybrid of a strictly time-independent and time-dependent calculation. In this way, it may provide a window for understanding the results of calculations which lie on either extreme. (Note that many calculations undertaken today under the "timedependent" label involve what might be considered a combination of time-dependent and time-independent methods using, e.g., grids for some of the degrees of freedom and basis sets for others. See, e.g., Ref. 35.)

The utility of a method which lies somewhere between the pure limits just discussed can be appreciated by considering Figs. 13 and 14. Figure 13 presents results for the propagation of the wave packet formed from the photodetachment process. The time-dependent propagation is estimated by expansion in the L^2 states using coefficients from the stick spectrum and the usual $\exp(-iEt/\hbar)$ phase factor. While it is clear from the pictures presented in Fig. 13 that the wave packet shows first rotational motion (at 30.00 fs) and then begins to move to larger values of R (90.0 fs and beyond), there is little specific information in the plots. The hierarchical decomposition provides a means to get more specific information and it does it in a manner which is nonparametric (e.g., we do not project onto a basis set). The plots in Sec. IV D make this clear. However, much of our analysis depends on the ability to plot a reasonable picture of the smoothed states, something which may be difficult for higher dimensional systems.

Figure 14 shows eigenstates from the L^2 calculation. These eigenstates are the full set used to generate the smoothed state on the lower left of Fig. 12, with one eigenstate in the sequence left out (296), because it has a very small coefficient. Figure 14 is presented to demonstrate that time-independent calculations on highly excited systems may yield complicated eigenstates which are difficult to interpret. However, it is clear that there are some simple states with high coefficients. For example, there is a set of states with high coefficients (283, 287, 293, and 298) which are a sequence of states with J=10 and increasing momentum along the R direction (more nodes). As noted earlier, such states give rise to smoothed states at higher levels of resolution than those shown in Sec. IV D. They can be viewed as progressions of "particle in the box" states. It is clear that the set of eigenstates (283, 287, 293, and 298) can be used in conjunction with the hierarchical analysis to label the peaks in Fig. 3(c) (the hierarchical analysis or something like it is needed to resolve the group 283-303). However, all the states pictured in Fig. 14 are unphysical in terms of the photodetachment process because they have the boundary conditions imposed by the L^2 calculation, showing once again the utility of generating smoothed states.

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