

## Structured photo-absorption spectra of ArHCl: fingerprints of overlapping broad resonances

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### Abstract

Thousands of complex-scaled, square-integrable overlapping diffraction resonances of ArHCl were calculated. About 300 of them were found to be sufficient to describe the photo-absorption spectra,  $\sigma_{\text{tot}}(E)$ , of ArHCl. It is first shown that their fingerprints may be seen in  $\sigma_{\text{tot}}(E)$ , even as structures which can not be explained by the reflection principle. It is shown here that the rate of decay of a single ArHCl resonance which has the largest overlap with the initial ground electronic state can be obtained through the extrapolation of the survival probability to  $t = 0$ . © 1998 Elsevier Science B.V. All rights reserved.

Resonances, as Taylor wrote in his book [1], are the most striking phenomenon in scattering theory. It is a common belief that the meaning of short-lived resonances is less physical and more technical in nature [2].

Here we show that this is not necessarily the case. Short-lived resonance poles of the scattering matrix are not quasistationary states, as the long-lived ones, but they are observable in the ArHCl case. As we show there are special structureless (without nodes) initial states of ArHCl which populate clusters of resonances that are far from one another in energy space and therefore lead to a structure in the photo-absorption spectra. This structure is a fingerprints of the overlapping short-lived resonances which can not

be expected on the basis of the reflection principle [3]. The fact that short-lived states are observable is encouraging. Mode selective chemistry is related to the question if it is possible to prepare selectively a system in one of two almost degenerate resonance states which are different in their lifetimes. Our work first shows that they can be distinguished if their symmetry allows it.

The selective population of the resonances is due to the symmetry properties of the resonances and the initial state. Time-dependent propagations can not provide us this information. Therefore, time-dependent simulations, which are commonly used nowadays for calculating the photo-absorption spectra, can not help us to design an experiment which is based on the symmetry properties of the resonances. For example, recent time-dependent calculations have shown that there is no structure in the photo-absorption of ArHCl which has been initially prepared in the ground electronic and vibrational state [4,5]. We

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obtained the same result from our time-independent calculations for the cross section, using the same potential energy surface as in Ref. [4,5] and by using the complex scaled square integrable resonance-poles of the scattering matrix as a basis set. However, analysis of the symmetry properties of the resonance wavefunctions enables us to propose another initial state which is also structureless but now the signature of the broad overlapping resonances pops out in the photo-absorption spectra of ArHCl.

Moreover, we show that for initial state which is a Gaussian superposition of the ArHCl overlapping resonances, the extrapolation to  $t = 0$  of the autocorrelation function (so called survival probability) provides the width (i.e. inverse lifetime) of the broad resonance which is the mostly populated state at  $t = 0$ . Therefore, even the lifetime of a specific broad ArHCl resonance is a measurable quantity although the ArHCl resonances overlap.

The structure in the photo-absorption spectra which is related to the broad resonances is *not* due to the almost vanishing denominator in the spectral representation of the Green operator as the energy gets close to a specific resonance-pole (this is the common case which is discussed in text books) but it is due to the vanishing numerator in the cross-section expression. This happens because of the special symmetry properties of the resonance wavefunctions and of the initial state.

Using the spectral representation of the Born–Oppenheimer Hamiltonian with the excited electronic potential energy surface, the photo-absorption cross section,  $\sigma_{\text{tot}}$  is expressed as [6,7]

$$\sigma_{\text{tot}}(E) \sim -\text{Im} \sum_n \frac{\langle\langle \Phi_0 | \psi_n^{\text{res}} \rangle\rangle \langle\langle \psi_n^{\text{res}} | \Phi_0 \rangle\rangle}{E - E_n} \quad (1)$$

where  $E_n = \mathcal{E}_n - \frac{i}{2}\Gamma_n$  are the eigenvalues of the complex scaled Hamiltonian which are associated with the poles of the S-matrix [8] whereas  $\psi_n^{\text{res}}$  are the corresponding eigen-states;  $\Phi_0$  is the product of the initial molecular state in the ground electronic state and the transition dipole moment function;  $\langle\langle \dots | \dots \rangle\rangle$  is the generalization of the inner product for the non-hermitian Hamiltonians [9].

Our approach is based on the fact that the motion of temporarily trapped hydrogen in between Ar and Cl (referred as the  $z$ -axis), at a given Ar–Cl distance, is much more rapid than its motion in a

direction which is perpendicular to the Ar–Cl axis. The adiabatic energy which is described as a function of the slow cylindrical coordinate  $\rho = \sqrt{(x^2 + y^2)}$  has a shape of an Eckart type potential barrier. Therefore, in spite of the fact that the excited electronic potential energy surface is a repulsive one,  $\text{ArHCl} \rightarrow \text{Ar} + \text{H} + \text{Cl}$ , thousands of  $J = 0$  resonances within the energy range of 1000–50000  $\text{cm}^{-1}$  with about the same short lifetime (inverse lifetime  $\approx 3000 \text{ cm}^{-1}$ ) were calculated using the complex coordinate method.

The 3D ArHCl resonances obtained by the adiabatic approach described above were found to be in a good agreement with the results obtained by us carrying out numerically exact calculations using the code we developed for any  $J = 0$ , 3D three body system. The advantage of the adiabatic approach is not only in providing insight into the dynamics but also in reducing the length of the calculations by several orders of magnitude. The results presented here are all obtained by the use of the adiabatic approach as described above.

The ArHCl resonances are associated with the oscillatory motion of hydrogen in between Ar and Cl (i.e. along the  $z$ -axis). Three good quantum numbers as the number of degrees of freedom of ArHCl ( $J = 0$ ) can be assigned to each one of the resonances. The first good quantum number is associated with the cylindrical radius coordinate  $\rho$ . The resonances possessing the same lowest quantum number,  $n_\rho = 1$ , have the smallest width (yet  $\Gamma \approx 3000 \text{ cm}^{-1}$ ) and are the only ones that contribute to the photo-dissociation dynamics.

In order to illustrate that the  $\approx 2000$  overlapping resonances (positions up to 50000  $\text{cm}^{-1}$ ) are assigned to the same given quantum number  $n_\rho = 1$  we calculated the probability of finding hydrogen on the surface of a cylinder with radius  $\rho$  for every one of these resonances.

Fig. 1 clearly shows that for all of them the largest probability of “finding” hydrogen is on a surface of a cylinder with the radius  $\rho = 0.6 \text{ au}$ . The standard deviation of  $\rho$  is about 0.27 au and becomes smaller as the scaling angle gets larger. This is due to the fact that upon complex scaling the resonances are described by localized square integrable functions [9]. Therefore, hydrogen “escapes” from the surface of a cylinder and *not* from the

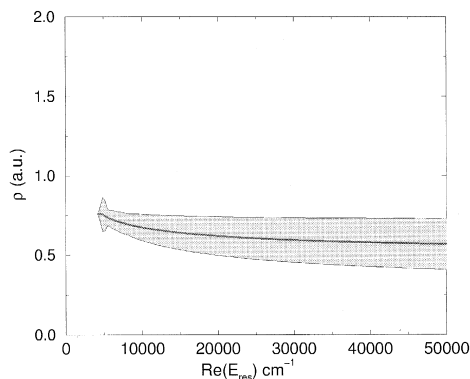


Fig. 1. The absolute value of the complex-expectation value of  $\langle\langle\Psi_{\text{res}}|\rho|\Psi_{\text{res}}\rangle\rangle \pm \Delta$  where  $\rho = \sqrt{x^2 + y^2}$  is perpendicular to the  $z$ -coordinate (hydrogen motion parallel to the Ar–Cl molecular axis),  $\Delta$  is the standard deviation and  $\Psi_{\text{res}}$  are the complex scaled  $\sim 2000$  overlapping resonances with about the same width of  $3000\text{cm}^{-1}$ .

Ar–Cl axis. The length of the cylinder depends on the averaged Ar–Cl distance at  $t = 0$ . The two other good quantum numbers which can be assigned to these broad overlapping resonances are  $n_z$  and  $n_R$ .  $n_z = 1, 2, \dots$  are associated with the quantized vibrational motion along the  $z$ -axis, where  $n_R = 1, 2, \dots$  stems from the effect of the almost-free-motion of the heavy atoms on the temporarily trapped motion

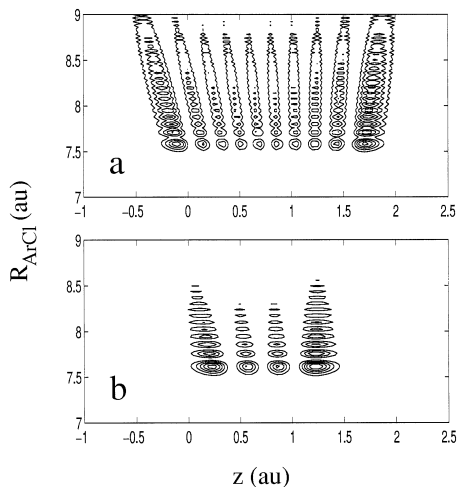


Fig. 2. The nodal structure of two representative ArHCl resonances as reflected in the probability distribution functions,  $|\Psi_{\text{res}}(\rho = 0.6, z, R_{\text{ArCl}})|^2 \rho$ . Energy position of resonance: (a)  $E = 33400\text{cm}^{-1}$ , (b)  $E = 19500\text{cm}^{-1}$ .

of hydrogen in between Ar and Cl. The clear nodal structure of resonances shown in Figs. 2a,b at  $\rho = 0.6$  au confirms the assignment of the resonances by the two good quantum numbers  $n_z$  and  $n_R$ .

One of the resonances presented in Fig. 2b is assigned by the  $n_z = 4$  quantum number, i.e. 3 nodes along  $z$ , and the other one (Fig. 2a) by the  $n_z = 10$  quantum number (9 nodes).

The resonance width, in a good approximation, varies linearly with the resonance position (i.e. energy). That is,  $\Gamma_n \approx \alpha E_n + \beta = 0.0393706 E_n + 0.00871423$  au, for the  $n$ -th resonance state. The resonance positions are about equally spaced by  $500\text{cm}^{-1}$ , i.e.  $E_n = E_0 + \Delta E n$ . For the initial state  $\Phi_0$ , where the resonances are populated with a Gaussian distribution centered at  $E_{n_0}$  (the Franck–Condon energy),  $n_0 \gg 0$  and with an exponential factor denoted by  $\gamma$ , the time derivative of the logarithm value of the survival probability  $S(t)$  is given by,

$$\left. \frac{d \ln S(t)}{dt} \right|_{t=0} = -i \langle\langle \Phi_0 | \hat{H}_{\text{cs}} | \Phi_0 \rangle\rangle \quad (2)$$

where  $\hat{H}_{\text{cs}}$  is the complex scaled Hamiltonian,  $\Phi_0$  is the complex scaled initial state and  $\langle\langle \dots | \dots \rangle\rangle$  is the c-product rather than the scalar inner product. Resonances are the eigenstates of this Hamiltonian, i.e.  $\hat{H}_{\text{cs}} \psi_n^{\text{res}} = (E_n - \frac{i}{2} \Gamma_n) \psi_n^{\text{res}}$ . Consequently  $\Phi_0$  can be expanded in the basis of the resonance wavefunctions:

$$\Phi_0 = \sum_n C_n \psi_n^{\text{res}}, \quad C_n^2 = N e^{-\gamma(n-n_0)^2} \quad (3)$$

where the normalization constant  $N$ , is chosen such that  $\sum_n C_n^2 = 1$ . It is easy to see that,

$$\begin{aligned} -2 \text{Re} \left. \frac{d \ln S(t)}{dt} \right|_{t=0} &= \sum_n C_n^2 \Gamma_n \\ &= \Gamma_{n_0} + \sum_n C_n^2 (\Gamma_n - \Gamma_{n_0}) \end{aligned} \quad (4)$$

substituting the expressions for  $\Gamma_n = \alpha E_n + \beta$  and  $E_n = E_0 + \Delta E n$  we obtain

$$\left. -2 \text{Re} \frac{d \ln S(t)}{dt} \right|_{t=0} = \Gamma_{n_0} + \alpha \Delta E \sum_n C_n^2 (n - n_0). \quad (5)$$

However,  $\sum_n C_n^2(n - n_0)$  is equal to zero since  $C_n^2$  is a Gaussian centered at  $n_0$ . Therefore,

$$-2 \operatorname{Re} \left. \frac{d \ln S(t)}{dt} \right|_{t=0} = \Gamma_{n_0}. \quad (6)$$

The conclusion is clear. Even when there is no structure in the ArHCl photo-absorption spectrum, the lifetime of a specific single resonance, denoted here by  $n_0$ , can be measured by taking the real part of the time derivative of the logarithm value of  $S(t)$  and by extrapolating it to  $t = 0$ . In Fig. 3 we represent the results obtained from the initial states that are Gaussian superposition (width of the Gaussian is  $5000 \text{ cm}^{-1}$ ) of overlapping resonances which correspond to the lowest vibrational state,  $n_z = 1$ , of the hydrogen in the Ar–Cl cage. As one can see the extrapolation of  $S(t)$  to  $t = 0$  enables us to determine the decay rate of two adjacent overlapping resonances ( $\Gamma \approx 3000 \text{ cm}^{-1}$ , difference in energy position  $\approx 500 \text{ cm}^{-1}$ ), although the initial states populate about 25 resonances.

The overlapping resonances which are populated during the Franck–Condon excitation are those located at the same region as  $\Phi_0$ . When  $\Phi_0$  is taken to be the ground electronic and vibrational wavefunc-

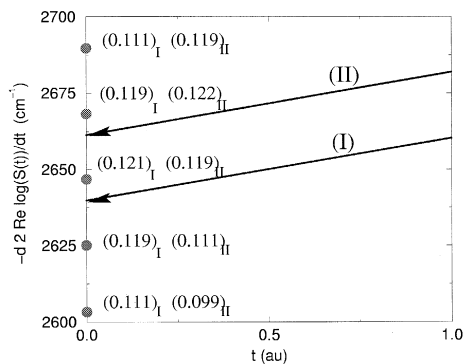


Fig. 3. The solid lines stand for the twice the real part of the time derivative of the logarithm value of the survival probability,  $S(t)$ , as obtained in our calculations for the initial states  $(\Phi_0)_I$  and  $(\Phi_0)_{II}$ .  $(\Phi_0)_I$  and  $(\Phi_0)_{II}$  are the Gaussian superpositions of the ArHCl overlapping resonances (associated with the lowest vibrational state  $n_z = 1$  of hydrogen in the ArCl cage) which are centered at two adjacent resonance states. The full circles represent the widths of the ArHCl resonances which are separated by  $\sim 500 \text{ cm}^{-1}$ . The population probabilities of these resonances by  $(\Phi_0)_I$  and  $(\Phi_0)_{II}$  are respectively given by  $(\dots)_I$  and  $(\dots)_{II}$ .

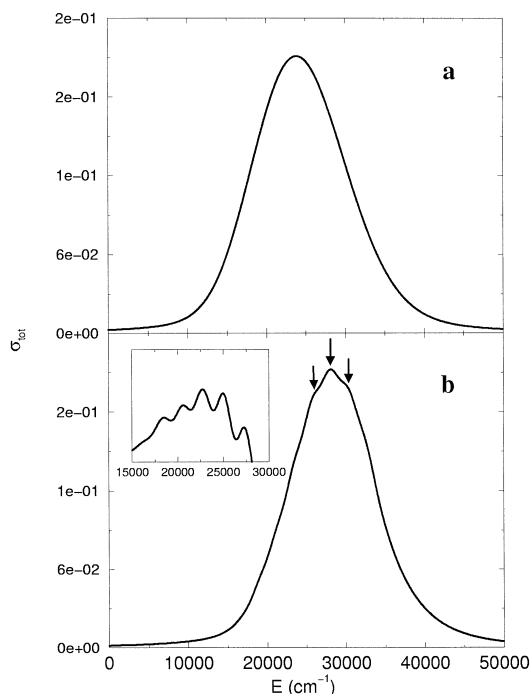


Fig. 4. The photo-absorption spectra of ArHCl when the initial state is: (a) the ground electronic and ground vibrational state of ArHCl, (b) the structureless wavefunction used by Bačić and co-workers [4,5] where the width of the Gaussian, which describes the ArCl coordinate, is reduced by the factor 13. Inset shows  $d\sigma/dE$  as function of  $E$ .

tion of ArHCl, a group of resonances with the energy position around  $25000 \text{ cm}^{-1}$  are populated during the excitation and indeed no structure in the photo-absorption spectrum has been observed, as one can see from the results presented in Fig. 4a (this result is in a complete agreement with the results obtained from time dependent calculations [4,5,10–13]).

In order to show that a structure in the photo-absorption spectrum due to the existence of broad overlapping resonances can be observed even when it is not expected on the basis of the reflection principle, we carried out a computational experiment where we used as the initial state the structureless wavefunction used by Bačić and co-workers [4,5], where the width of the Gaussian, which describes the ArCl coordinate, is reduced by a factor of 13. In such a case, in the Franck–Condon excitation experiment, only the resonances which are localized around

the equilibrium distance of ArCl in ArHCl complex are populated (although on the upper potential energy surface Ar and Cl move almost freely). This selective population of the overlapping resonances leads to the structure in the photoabsorption spectrum which is presented in Fig. 4b. The arrows in Fig. 4b and the  $d\sigma/dE$  plot emphasize the structure with about  $2000\text{ cm}^{-1}$  spacing between the peaks. This is the frequency of hydrogen which vibrates in between Ar and Cl along the  $z$ -axis and is a quantum version of the “cage effect” mentioned by Gerber and his co-workers [10–13]. This is a clear numerical proof that the “fingerprints” of the overlapping resonances of ArHCl can be seen in the photoabsorption spectrum even for the structureless initial state. The possibility of observing such a spectrum in experiment depends on the ability of preparing an initial narrow wave-packet on the ground electronic potential energy surface, as proposed above. There are, however, other systems which have a similar dynamical behavior but are more suitable for experimental studies. Such are the electronically excited HCl which is adsorbed on the MgO surface [14,15], or in a dimer in the gas phase. The dynamics of these two systems are under current theoretical study using the same theoretical approach presented here.

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