Vibrational predissociation in the HCl dimer

G. W. M. Vissers
Institute of Theoretical Chemistry, NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

L. Oudejans and R. E. Miller
Department of Chemistry, University of North-Carolina, Chapel Hill, North Carolina 27599

G. C. Groenenboom and A. van der Avoird
Institute of Theoretical Chemistry, NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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We present results of a combined theoretical and experimental study on the vibrational predissociation of the HCl dimer. On the theoretical side, photodissociation linewidths and product-state distributions for monomer stretch excited states with total angular momentum \( J = 0 \) were computed, using the Fermi golden rule approximation. The resonances investigated include excitation of the hydrogen bond donor and acceptor stretches, as well as combinations of one of these modes with the intermolecular stretch and geared bend modes, for both even and odd permutation symmetry. Line strengths for the transitions from the \( J = 1, K = 0 \) ground state to excited states with \( J = 0 \) were computed using quasibound states. On the experimental side, the photofragment angular distribution method was employed to obtain complete final-state distributions for the monomer stretch excited states. Three different transitions were probed, all starting from the lower tunneling component of the ground state: the \( R_{Q0}(1) \) transition for excitation of the acceptor stretch and the \( Q_{R0}(0) \) transition and unresolved \( Q_{R0} \) branch for the donor stretch excitation. We find that, in contrast to the HF dimer, the excited-state alignment of the HCl dimer, resulting from excitation using a polarized laser beam, is completely lost on the time scale of the dissociation. The agreement between theory and experiment for the product-state distributions and line strengths is reasonable. The computed lifetimes are \( 1 \)–\( 2 \) orders of magnitude too small, which is attributed to a deficiency in the potential energy surface. © 2004 American Institute of Physics. [DOI: 10.1063/1.1711601]

I. INTRODUCTION

Hydrogen bonding is one of the most important interactions in nature. It is studied in many areas of science, ranging from chemistry and physics to biology. For a quantitative description of such a bond, it is helpful to study small model systems. The simplest of these are hydrogen halide dimers, such as (HF)\(_2\) and (HCl)\(_2\). In the past few decades, considerable progress has been made in the description of these systems, both experimentally\(^1\)–\(^10\) and theoretically\(^11\)–\(^22\).

Despite the obvious similarities between (HF)\(_2\) and (HCl)\(_2\), it is well known that their vibrational dynamics are quite different. For example, although both of these systems consist of a proton-acceptor–proton-donor pair, the HCl dimer has been shown both spectroscopically\(^1\),\(^3\)–\(^5\),\(^9\),\(^23\),\(^24\) and theoretically\(^11\),\(^12\),\(^14\)–\(^16\),\(^25\)–\(^27\) to be much floppier than HF dimer. This is illustrated by the fact that the geared tunneling frequency in the ground state of the HF dimer is 0.66 cm\(^{-1}\)\(^\text{a}\),\(^6\),\(^7\) while the corresponding value for the HCl dimer is as large as 15.5 cm\(^{-1}\)\(^\text{a}\),\(^4\),\(^9\). Since this value is comparable to the rotational energy spacing \( (j = 1 \rightarrow 0) \) in the monomer (21 cm\(^{-1}\)), it seems that the HCl molecules undergo nearly free rotation in the dimer. This is consistent with the observation that the dissociation energy of the HCl dimer is much lower \([439 \pm 1 \text{ cm}^{-1} \text{ (Ref. 28)}]\) than that of the HF dimer \([1062 \pm 2 \text{ cm}^{-1} \text{ (Ref. 29)}]\).

This paper deals with the vibrational predissociation of the HCl dimer. Although there are a large number of papers on the vibrational predissociation of the HF dimer,\(^21\),\(^29\)–\(^42\) the corresponding data set for the HCl dimer is rather small. While there are a number of experimental studies that have been published,\(^28\),\(^43\)–\(^48\) theoretical efforts have been restricted to bound-state calculations of the vibration–rotation–tunneling levels of the HCl stretch excited dimer.\(^15\). To our knowledge, no theoretical description of the photodissociation of monomer stretch excited (HCl)\(_2\) has been published.

The dramatic difference in the tunneling rates for HF and HCl dimers is potentially of great significance with regard to the associated vibrational predissociation dynamics. In several previous publications\(^28\),\(^36\),\(^42\) it was shown that the final HF-fragment rotational-state distribution resulting from vibrational predissociation of HF dimer can be understood in terms of the asymmetric equilibrium structure, which makes the proton donor and acceptor molecules in the parent complex quite different. In particular, the proton donor molecule receives a large torque as the molecules recoil, while the...

\(^{a}\)Current address: Arcadis G&M, Inc., P.O. Box 13109, Research Triangle Park, NC 27709.
force on the proton acceptor acts nearly through its center of mass. In view of the qualitatively different tunneling dynamics associated with the HCl dimer, we were interested in exploring the effects this has on the associated vibrational predissociation dynamics.

In this paper, we present the results of full-dimensional [six-dimensional (6D)] quantum calculations on the vibrational predissociation of the H\textsuperscript{35}Cl dimer, for total angular momentum $J=0$. In a previous study on the vibrational predissociation of HF dimer it was shown that the Fermi golden rule approximation gives linewidths and product-state distributions that are in good agreement with full coupled channels calculations.\textsuperscript{42} The same study also showed that the use of quasibound states to compute line strengths for the transitions to the vibrationally predissociating states is justified. We therefore applied the same approximations to the HCl dimer. We report lifetimes and rotational-state distributions for the hydrogen bond acceptor and donor stretch modes, as well as for combinations of these excitations with an in-plane oscillation.\textsuperscript{49} The angular part of the interaction potential is expanded in functions of the type of Eq. (\ref{e:innov}).

The dimer stretch basis functions are given by

\begin{equation}
  \langle j_A j_B K;JM \rangle = \sqrt{\frac{2J+1}{4\pi}} D_{MK}^{(J)}(\alpha,\beta,0)^* \times \sum_{m_A m_B} |j_A m_A| |j_B m_B\rangle \langle j_A m_A j_B m_B| j_A j_B K\rangle,
\end{equation}

with $|j_X m_X\rangle = Y_{m_X}^{(j_X)}(\hat{R}_{x})$ spherical harmonics, coupled by a Clebsch–Gordan coefficient $\langle j_A m_A j_B m_B| j_A j_B K\rangle$. The Wigner rotation function $D_{MK}^{(J)}(\alpha,\beta,0)^*$ depends on the polar angles $(\beta,\alpha)$ of the intermolecular vector $\hat{R}$ with respect to a space-fixed frame.

The dimer stretch basis functions are given by $\varphi_\alpha(R) = \varphi_\alpha(R)/R$, where the $\varphi_\alpha(R)$ are eigenfunctions of a reference Hamiltonian

\begin{equation}
  \hat{h}^\text{ref} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V^\text{ref}(R).
\end{equation}

The reference potential $V^\text{ref}(R)$ is obtained by minimizing the full 6D potential in all coordinates but $R$. The eigenfunctions of $\hat{h}^\text{ref}$ are also computed using a sinc function DVR.

The angular part of the interaction potential is expanded in functions of the type of Eq. (\ref{e:innov}), with expansion coefficients depending on $r_A$, $r_B$, and $R$. Since the potential is invariant under overall rotations of the system, it does not depend on $\alpha$ and $\beta$ or on $\phi_A$ and $\phi_B$ separately, but only on the difference angle $\phi = \phi_B - \phi_A$. Hence only the terms with $J=K=0$ appear in the expansion, so that the expansion functions for the potential can be written

\begin{equation}
  A_{L_A L_B L} = (-1)^{L_A+L_B+L} \times \sum_{M_A} \begin{vmatrix} L_A & L_B & L \\ M_A & -M_A & 0 \end{vmatrix} |L_A M_A\rangle |L_B M_B\rangle.
\end{equation}

In our work on the infrared photodissociation of the HF dimer, we found that the Fermi golden rule approximation gives lifetimes and rotational-state distributions which are in good agreement with a full coupled channels calculation.\textsuperscript{50} We will therefore apply this approximation also to the HCl–HCl system. In the golden rule approximation, the linewidth $\Gamma$ of a resonance is given by

\begin{equation}
  \Gamma = \frac{\pi}{\hbar} \sum_{\alpha} \frac{1}{2} |\langle \alpha | \Delta \hat{H} | \alpha \rangle|^2 \delta \Omega_{\alpha},
\end{equation}

where $\Delta \hat{H}$ is the total angular momentum of the dimer and $\hat{J}_{AB}$ is the vector sum of the monomer angular momentum operators $\hat{j}_A$ and $\hat{j}_B$.
\[ \Gamma = \sum_{j_a j_B} \Gamma_{j_a j_B} = \sum_{j_a j_B} \frac{2\pi}{\hbar} |\langle \psi_{jM} | V_{10} | \psi_{JM}^{(-1)} j_a j_B^{AB} \rangle|^2, \]

where the \( V_{10} \) is the vibrational coupling potential between HCl-stretch excited- \((v_A + v_B = 1)\) and ground- \((v_A = v_B = 0)\) state basis functions. The bound state \(| \psi_{jM} \rangle\) is calculated in a basis without the ground-state functions, and \( \psi_{JM}^{(-1)} j_a j_B^{AB} \) is the energy normalized scattering wave function calculated in a basis with ground-state HCl-stretch functions only. The rotational-state distribution can be defined as the ratio of the partial linewidths to the total linewidth:

\[ P_{j_a j_B} = \frac{\Gamma_{j_a j_B}}{\Gamma}. \]

As in our work on the photodissociation of the HF dimer,\(^{42}\) the scattering wave function \( \psi_{JM}^{(-1)} j_a j_B^{AB} \) is expanded in a space-fixed basis \(|(j_a j_B)_{AB}^{1}; JM \rangle^{SF}\), which is related to the body-fixed basis via a unitary transformation:

\[ \sum_{K} |(j_a j_B)_{AB}^{1}; JM \rangle \langle K; JM| \sum_{K} |(j_a j_B)_{AB}^{1}; JM \rangle^{SF}, \]

Using the expansion

\[ \psi_{JM}^{(-1)} j_a j_B^{AB} (R, r_A, r_B) = \sum_{v_A v_B, l_a l_B} R^{-1} f_{v_A v_B, l_a l_B}^{j_a j_B} (R) \times |(j_a j_B)_{AB}^{1}; JM \rangle^{SF}, \]

the expansion coefficients \( f_{v_A v_B, l_a l_B}^{j_a j_B} (R) \) can for large \( R \) be written as

\[ f_{v_A v_B, l_a l_B}^{j_a j_B} (R) = \frac{1}{\sqrt{2\pi \hbar}} \left[ \delta_{\ell a} \delta_{\ell b} \delta_{l_B} \delta_{l_B} \delta_{l_B} \right], \]

where \( S \) is the scattering matrix.\(^{51}\) The flux normalized outgoing waves \( v_{v_A v_B, l_a l_B}^{j_a j_B} (R) \) and incoming waves \( u_{v_A v_B, l_a l_B}^{j_a j_B} (R) \) are given by

\[ u_{v_A v_B, l_a l_B}^{j_a j_B} (R) = i \sqrt{\frac{\mu k}{\hbar}} R^{(1)} (k_{v_A v_B, l_a l_B}^{j_a j_B} R), \]

\[ u_{v_A v_B, l_a l_B}^{j_a j_B} (R) = -i \sqrt{\frac{\mu k}{\hbar}} R^{(2)} (k_{v_A v_B, l_a l_B}^{j_a j_B} R) \]

where \( R^{(1)} \) and \( R^{(2)} \) are spherical Hankel functions of the first and second kind,\(^{52}\) respectively, and where the wave numbers \( k_{v_A v_B, l_a l_B}^{j_a j_B} \) are defined as

\[ k_{v_A v_B, l_a l_B}^{j_a j_B} = \sqrt{\frac{2\mu (E - e_{v_A} - e_{v_B})}{\hbar^2}}. \]

### III. Computational Details

The ES1–EL (Ref. 16) potential energy surface was used in the present calculation. This potential surface is based on the earlier ES1 potential\(^{14}\) by Elrod and Saykally. The ES1 potential is fit to a large amount of spectroscopic data, with an earlier ab initio potential by Bunker et al.\(^{2}\) as a starting point. However, this fit used four-dimensional calculations (i.e., excluding the monomer vibrations) to modify only some of the intermolecular parameters, while leaving the intramolecular parameters untouched. In the ab initio potential and, consequently, also in the ES1 potential, the dependence on the monomer stretch coordinates was found to be much too weak. This problem was partially solved in an ad hoc manner by Qiu et al. with the addition of an electrostatic interaction potential, leading to the ES1–EL potential.\(^{16}\) This relatively simple modification gave tunneling splittings in the monomer stretch excited state that were in much better agreement with experiment (see Table I for a number of relevant parameters). We expanded this potential in terms of angular functions of Eq. (5) up to \( L_a = L_B = 13\).

The quasibound-state wave functions and energies have been calculated in a basis with \( j_a j_B = 13, v_A + v_B = 2, \) and \( n = 8, \) giving a basis of approximately 28,500 functions. This was found to be sufficient to converge the energies to within 0.01 cm\(^{-1}\). The monomer eigenfunctions were calculated using a sine function DVR on an equally spaced grid of 35 points in the range \((1.6 – 3.7)\) \(\alpha_0\). For the dimer stretch basis functions, an equally spaced grid of 185 points between \(6\alpha_0\) and \(11\alpha_0\) was used. To compute the monomer stretch excited states, a three-step diagonalization of the Hamiltonian was used, which is described in our paper on the bound states of the HF dimer.\(^{50}\)

The bound state \(| \psi_{jM} \rangle\) in the golden rule expression was calculated in a basis with \( v_A + v_B = 1, j_a j_B = 13, \) and \( n = 8. \) The radial scattering wave function was represented on an equally spaced 332-point grid, in the range \((3 – 21)\) \(\alpha_0\). A renormalized Numerov\(^{35}\) propagator was used to compute this wave function. The radial integral was built up in parallel to the propagation, using a method similar to that described by Gadéa et al.\(^{54}\) In the propagation, the scattering wave function was represented in the body-fixed basis; the transformation to the space-fixed basis was not performed until the matching of the wave function to the asymptotic
solutions. Rotational channels up to \( j_A, j_B = 16 \) were used to describe the scattering wave function, giving a total of \( \approx 800 \) dissociation channels for scattering states of odd exchange symmetry and \( \approx 1000 \) channels for the even states. About half of the available channels were open in the investigated energy range, up to \( (j_A, j_B) = (2, 15) \) for the resonance highest in energy \( (\nu_1 + \nu_3) \).

In the calculation of the line strengths of the transitions, the dimer dipole moment was approximated by the sum of the vibrational transition dipole moments of the monomers, \( \langle 1 \mu_{\text{HCl}} | 0 \rangle \). The same approximation was used for the HF dimer, and matrix elements for the dimer transition dipole in the basis of Eq. (2) are given there.

### IV. Experimental Method

The experimental method used in this study has been discussed in detail elsewhere. Rotatable molecular beam source that is collimated by two skimmers to provide high angular resolution. The HCl dimer was formed by expanding a 5% mixture of HCl in helium through a (room-temperature) 50-\( \mu \)m-diam nozzle from a source pressure of 600 kPa. In addition, a mix with 20% of the amount of helium replaced by argon was used to reduce the beam velocity, enhancing the angular resolution. Since the near-infrared spectrum of the HCl dimer is well known, the measured velocity for the 5% HCl in a He mixture of 1465 and 995 m/s for the (20% argon)/(5% HCl) in the helium mixture. These values are in good agreement with those estimated from the percentage weighted mass of the expanding gas: namely, 1480 and 980 m/s, respectively.

### V. Results

#### A. Calculations

The monomer stretch excitations are labeled \( \nu_1 \) for excitation of the hydrogen bond acceptor (the “free” HCl molecule) and \( \nu_2 \) for excitation of the donor (the “bound” molecule). The intermolecular modes are \( \nu_4 \) for excitation of the dimer stretch and \( \nu_5 \) for the in-plane geared bend. The calculations were performed for \( \nu_1 \), \( \nu_1 + \nu_4 \), \( \nu_1 + \nu_5 \), \( \nu_2 \), \( \nu_4 \), and \( \nu_5 \) modes, for total angular momentum \( J = 0 \) and for both even \( (A_1) \) and odd \( (B_2) \) states with respect to monomer exchange. The computed predissociating states are all even with respect to spatial inversion. Following normal conventions in IR spectroscopy, we will also label transitions to excited states of \( B_2 \) symmetry with \( \nu^+ \) and transitions to states of \( A_1 \) symmetry with \( \nu^- \). The calculated energies of the quasibound states studied in this paper are given in Table II, together with the available experimental frequencies. The calculated values given here are nearly identical to those reported by Qiu et al. using the same potential energy surface (PES).

The theoretical linewidths, computed at the quasibound-state energies, are given in Table III. Comparison with the experimental linewidths shows that the theoretical values with the ES1–EL potential are 1–2 orders of magnitude too small. A problem in the calculation of the linewidths is the strong dependence of the linewidth on the total energy at which the golden rule calculation is performed. An extreme example of this can be seen in Fig. 2, where the linewidth for the \( \nu_1 \) excitation is plotted for a range of energies around the resonance frequency. The calculated linewidths are all even with respect to spatial inversion. Following normal conventions in IR spectroscopy, we will also label transitions to excited states of \( B_2 \) symmetry with \( \nu^+ \) and transitions to states of \( A_1 \) symmetry with \( \nu^- \). The calculated energies of the quasibound states studied in this paper are given in Table II, together with the available experimental frequencies. The calculated values given here are nearly identical to those reported by Qiu et al. using the same potential energy surface (PES).

### Table II. Quasibound state energies of the HCl dimer, in cm\(^{-1}\). All resonance frequencies are relative to the ground state.

<table>
<thead>
<tr>
<th>( A_1 )</th>
<th>( B_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>2876.69</td>
</tr>
<tr>
<td>( \nu_1 + \nu_4 )</td>
<td>2942.53</td>
</tr>
<tr>
<td>( \nu_1 + \nu_5 )</td>
<td>2967.23</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>2857.01</td>
</tr>
<tr>
<td>( \nu_2 + \nu_4 )</td>
<td>2931.99</td>
</tr>
<tr>
<td>( \nu_2 + \nu_5 )</td>
<td>2912.57</td>
</tr>
</tbody>
</table>

\(^a\)Reference 44.
\(^b\)References 4 and 47.
\(^c\)Reference 47.
likely due to a rotational resonance, an effect that was observed previously in the vibrational predissociation of the Ar–CH₄ complex. However, we were unable to analyze this resonance due to the large number of rotational channels involved. Note that for this resonance, the discrepancy with experiment is even worse if the golden rule calculation is done at a different energy.

The rotational-state distributions of the fragments are much less dependent on the energy at which the computation is performed. Whereas the linewidth can change dramatically over a range of 1–2 cm⁻¹, these distributions remain fairly constant over the same range. Therefore it is safe to discuss particular features found in these distributions. We will label the dissociation channels with a pair of rotational quantum numbers \((j_1, j_2)\), which denotes a symmetrized combination of basis functions with \((j_A, j_B) = (j_1, j_2)\) and \((j_A, j_B) = (j_2, j_1)\).

Figure 3 shows the rotational-state distributions \((j_1, j_2)\) for the \(v_2\) and \(v_1\) scattering states of \(A_1\) symmetry. An overview of the most important contributions to the rotational-state distributions for all the resonances investigated is given in Tables IV and V. The most striking feature is the high contribution of the lower rotational channels to the distribution of the \(n_2\) excited state. This is in stark contrast with the \(n_1\) resonance of the same symmetry, where the contribution from these product channels is negligible. Instead, nearly all photofragments end up in the higher rotational channels for this resonance, with nearly half of them in the highest open channel: namely, \(4, 14\).

Inspection of the distributions for the other states shows that there are more excitations for which the contribution of the lower rotational channels is significant. These are the \((n_2 + n_4)\)⁻ and \((n_2 + n_5)\)⁻ resonances and, to a lesser extent, the \((n_1 + n_4)\)⁻ and \((n_2 + n_4)\)⁺ resonances. In comparison, the larger anisotropy associated with the HF dimer results in all HF fragments being produced in highly rotationally excited channels. This is consistent with earlier studies, which show that not only is the HCl–HCl hydrogen bond weaker than that in the HF dimer, it is also less directional.

Using a quasibound-state approximation to the excited states, we computed the line strengths for transitions from the \(J=1, K=0\) ground state to the \(J=0\) predissociating states, as summarized in Table VI. The symmetry labels in

**TABLE III. Vibrational predissociation linewidths \(\Gamma\), in MHz.** The experimental linewidths reported for Ref. 28 have been calculated from the lifetimes which were measured directly in a time resolved, pulsed laser experiment.

<table>
<thead>
<tr>
<th>(A_1)</th>
<th>(B_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_1)</td>
<td>(0.1074)</td>
</tr>
<tr>
<td>(n_1 + n_4)</td>
<td>(0.0473)</td>
</tr>
<tr>
<td>(n_1 + n_4)</td>
<td>(0.0296)</td>
</tr>
<tr>
<td>(n_2)</td>
<td>(0.0366)</td>
</tr>
<tr>
<td>(n_2 + n_4)</td>
<td>(0.1516)</td>
</tr>
<tr>
<td>(n_2 + n_4)</td>
<td>(0.0574)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 28.
\(^b\)Reference 44.
\(^c\)Reference 47.
their transition moments to the symmetry of the excited states. Selection rules imply that only transitions from the upper tunneling level of the \( J = 1, K = 0 \) ground state (having \( A_1 \) symmetry) to the \( A_1 \) excited states and from the lower ground-state tunneling level (of \( B_1 \) symmetry) to the \( B_2 \) excited states are allowed.

**B. Experiments**

1. **Acceptor stretch \( v_1 \)**

From the previous infrared study of the HCl dimer \(^{44}\) we know that the highest-frequency vibrational band with high intensity is located at 2890 cm\(^{-1}\), corresponding to the \( K_a = 1 \leftarrow 0 \) subband of the \( v_1 \) vibration, starting from the lower tunneling state. The dominant features in this spectral region are the three \( Q \) branches associated with the three dimer isotopic modifications: namely, (H\(^{35}\)Cl)\(_2\), H\(^{35}\)Cl–H\(^{37}\)Cl, and (H\(^{37}\)Cl)\(_2\). From earlier studies on the HF dimer \(^{35}\) we know that the best possible resolution of the individual fragment states is found when the \( R \) transition is excited with the laser polarization direction parallel to the velocity vector of the parent molecule, assuming that the complex dissociates along its \( A \) axis. This is a result of the fact that this polarization selectively excites those molecules with their transition moments (approximately perpendicular to their \( A \) axis) aligned parallel to the molecular beam direction. As a result, the fragments tend to scatter primarily to the maximum possible scattering angle and do not contribute to the signal at smaller angles, where the lower recoil energy fragments appear. Figure 4(a) shows the resulting angular distribution with parallel polarization. Although individual rotational channels are more closely spaced in angle than for HF dimer, owing to the larger mass of the HCl fragments, there is still some structure in the angular distribution, with clear evidence for at least three separate channels.

Before discussing the fitting of this angular distribution, it is helpful to consider the case when the polarization is directed perpendicular to the parent molecule velocity vector—i.e., perpendicular to the molecular beam. This angular distribution is shown in Fig. 4(b) and within the experimental uncertainties is identical to that obtained with parallel polarization. This is in stark contrast to the HF dimer \(^{29}\) and other systems we have studied \(^{56,57}\) where the perpendicular polarization gives an angular distribution that is much more forward peaked, since now we selectively excite the parent molecules that are aligned with their transition moments perpendicular to the beam axis, which in the axial recoil limit would tend to give fragments that recoil near zero degrees. One obvious explanation for this would be that the system does not dissociate axially. However, before we can draw

**TABLE IV.** Overview of the most important contributions (highest probabilities) to the rotational state distributions, for scattering states of \( A_1 \) symmetry. The last two lines show the distribution of the excess energy, in cm\(^{-1}\), over rotational and translation energy of the fragments. All values are percentages.

<table>
<thead>
<tr>
<th>((j_A, j_B))</th>
<th>(v_1^A)</th>
<th>((v_1 + v_3)^A)</th>
<th>((v_1 + v_3)^B)</th>
<th>(v_2^B)</th>
<th>((v_2 + v_3)^B)</th>
<th>((v_2 + v_3)^A)</th>
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<tbody>
<tr>
<td>(0,0)</td>
<td>0.02</td>
<td>0.01</td>
<td>0.17</td>
<td>7.37</td>
<td>1.28</td>
<td>1.62</td>
</tr>
<tr>
<td>(8,11)</td>
<td>3.18</td>
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<tr>
<td>(2,14)</td>
<td>3.17</td>
<td>2.73</td>
<td>0.49</td>
<td>2.08</td>
<td>0.16</td>
<td>5.47</td>
</tr>
<tr>
<td>(10,10)</td>
<td>7.03</td>
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<td>(3,14)</td>
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<td>6.10</td>
<td>1.98</td>
<td>13.00</td>
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<td>1.57</td>
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<td>0.00</td>
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</tr>
<tr>
<td>(E_{\text{rot}})</td>
<td>91.30</td>
<td>88.94</td>
<td>92.48</td>
<td>70.76</td>
<td>88.02</td>
<td>74.29</td>
</tr>
<tr>
<td>(E_{\text{trans}})</td>
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<td>11.06</td>
<td>7.52</td>
<td>29.24</td>
<td>11.98</td>
<td>25.71</td>
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</table>

**TABLE V.** As Table IV, for scattering states of \( B_2 \) symmetry.

<table>
<thead>
<tr>
<th>((j_A, j_B))</th>
<th>(v_1^A)</th>
<th>((v_1 + v_3)^A)</th>
<th>((v_1 + v_3)^B)</th>
<th>(v_2^B)</th>
<th>((v_2 + v_3)^B)</th>
<th>((v_2 + v_3)^A)</th>
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<tbody>
<tr>
<td>(5,13)</td>
<td>6.42</td>
<td>5.51</td>
<td>0.14</td>
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<td>2.90</td>
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<tr>
<td>(3,14)</td>
<td>6.24</td>
<td>2.99</td>
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<td>0.84</td>
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<td>(9,11)</td>
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<td>3.95</td>
<td>1.98</td>
</tr>
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<td>7.08</td>
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<td>11.54</td>
<td>2.49</td>
<td>2.47</td>
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<tr>
<td>(8,12)</td>
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<td>2.11</td>
<td>27.38</td>
<td>13.24</td>
<td>15.75</td>
</tr>
<tr>
<td>(4,14)</td>
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<td>3.24</td>
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<td>(10,11)</td>
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<tr>
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<td>95.40</td>
<td>88.94</td>
<td>86.08</td>
<td>89.69</td>
</tr>
<tr>
<td>(E_{\text{trans}})</td>
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<td>11.02</td>
<td>4.60</td>
<td>11.06</td>
<td>13.91</td>
<td>10.31</td>
</tr>
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</table>
such a conclusion we need to consider the possibility that the alignment that is initially imposed on the system by excitation with a linearly polarized laser is lost before the molecule dissociates. There are two reasons we might expect such behavior. First, as already documented in the literature, the predissociation lifetimes of the HCl dimer are considerably longer than those of HF dimer, giving the system more time to lose this alignment. In addition, the nuclear hyperfine splitting is very large in HCl, as indicated above, such that the nuclear hyperfine depolarization should be much faster than in HF dimer. In our earlier estimate for HF dimer we determined that the lifetime was much shorter than the depolarization time by 4 orders of magnitude. For the HCl dimer, however, we estimate that the lifetime is approximately equal to the depolarization time, based on the electric quadrupole coupling constant of the chlorine: namely, approximately 68 MHz and a lifetime of the $n=1$ HCl dimer of approximately 100 ns.

A further test that the detailed shape of the angular distributions is independent of the initial alignment imposed by the excitation process comes from recording the angular distribution while having the laser tuned to the center of the largest peak in the $Q$ branch. This angular distribution, shown in Fig. 4, is identical to the other two within the experimental uncertainty. As a result of these measurements, we conclude that the alignment is completely lost on the time scale for dissociation of the complex, which means that we cannot use the polarization method to determine whether or not the molecule dissociates in an axial fashion. In view of this, all the fits to the experimental angular distributions were carried out using an anisotropy parameter $\beta = 0$.

The next step would be to obtain an angular distribution for the upper tunneling state of the $n=1$ stretch. Unfortunately, the large tunneling splitting in the vibrational ground state ($\sim 15.5 \text{ cm}^{-1}$), combined with the low rotational temperature of the molecular beam, made the signals for this state too low for detailed analysis.

As mentioned above, the heavy mass of the HCl fragment restricts the angular distributions to angles smaller than $17^\circ$. In an attempt to improve the angular resolution we also recorded angular distributions for the $\nu_1^+ R_{0}(1)$ transition splitting is very large in HCl, as indicated above, such that the nuclear hyperfine depolarization should be much faster than in HF dimer. In our earlier estimate for HF dimer we determined that the lifetime was much shorter than the depolarization time (by 4 orders of magnitude). For the HCl dimer, however, we estimate that the lifetime is approximately equal to the depolarization time, based on the electric quadrupole coupling constant of the chlorine: namely, approximately 68 MHz (Refs. 58 and 59) and a lifetime of the $n=1$ HCl dimer of approximately 100 ns (linewidth: 1.6 MHz). A further test that the detailed shape of the angular distributions is independent of the initial alignment imposed by the excitation process comes from recording the angular distribution while having the laser tuned to the center of the largest peak in the $Q$ branch. This angular distribution, shown in Fig. 4, is identical to the other two within the experimental uncertainty. As a result of these measurements, we conclude that the alignment is completely lost on the time scale for dissociation of the complex, which means that we cannot use the polarization method to determine whether or not the molecule dissociates in an axial fashion. In view of this, all the fits to the experimental angular distributions were carried out using an anisotropy parameter $\beta = 0$.

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using a gas mixture containing 20% argon. The lower velocity of the resulting molecular beam spreads out the angular distribution to 25°, as shown in the inset in Fig. 5.

The angular distributions obtained for the other two isotopic forms of the dimer were indistinguishable from those shown above. As a result, we present here only an analysis of the H\(^{35}\)Cl dimer. It is interesting to note, however, that the situation is quite different for the HF–HCl complex,\(^{57,60}\) where both the lifetimes and final-state distributions are dependent upon the chlorine isotope.

2. Donor stretch \(\nu_2\)

The “bound” HCl stretch is further redshifted from the HCl monomer, which makes it even more difficult to reach with the F-center laser. Nevertheless, we were successful in getting the laser to operate single mode at the appropriate frequency to observe the unresolved \(Q\) branch belonging to the \(K_a=1\leftarrow 0\) subband at 2868.15 cm\(^{-1}\) as well as the \(K_a=0\leftarrow 0\) subband transitions at 2857 cm\(^{-1}\). This provides us with a unique opportunity to observe possible differences in the dynamics of the photodissociation upon excitation of an additional \(\text{HCl}\) quantum, within the same vibrational band.

Figure 6(a) shows an angular distribution obtained with the laser tuned to the top of the unresolved \(Q\) branch in the \(K_a=1\leftarrow 0\) while in Fig. 6(b) the angular distribution for the \(R(0), K_a=0\leftarrow 0\) transition is shown. The angular distributions recorded in this way show no dependence on polarization direction, indicating once again that hyperfine depolarization is fast with respect to the dissociation lifetime. Again, we find that the angular distribution for all of the other isotopomers of the dimer in the \(K_a=0\leftarrow 0\) subband are the same within the experimental uncertainty. Overall, the angular distribution is quite similar to that obtained from excitation of the “free” HCl stretch. However, due to the somewhat smaller excitation energy associated with the “bound” stretch, in comparison with the “free” stretch, the first peak in the angular distribution of the former appears at somewhat smaller angles than for the latter. Once again, transitions starting from the upper tunneling state were too weak for detailed analysis.

VI. DISCUSSION

A. Analysis of the angular distributions

Before discussing the assignment of the features in the angular distributions presented above, it is important to consider what is already known about the dissociation of the HCl dimer. First, the study of Pine and Howard\(^3\) provides a reasonable estimate of the dissociation energy \(D_0\) of this complex: namely, 431±22 cm\(^{-1}\). This is extremely helpful since it defines, at least approximately, which channels are available. More recently, Ni \textit{et al.}\(^{28}\) obtained a more accurate value of \(D_0=439\pm 1\) cm\(^{-1}\). Figure 7 shows an energy level diagram for the HCl dimer, using this value for the dissociation energy. It is interesting to note the rather large energy gap between the available energy and the first open channel. This is clearly consistent with the fact that the first peak in the experimental angular distributions appears at 5.8° following excitation of the “free” \(\nu_1\) HCl stretch, corresponding to a recoil energy of 74 cm\(^{-1}\). The additional structure in the angular distribution is associated with the other rotational channels in Fig. 7. Careful examination of the angular positions of the peaks in the experiment is consistent with a dissociation energy of 439 cm\(^{-1}\). Unfortunately, as can be seen from Fig. 7, several open channels are rather closely spaced, including the first two open channels—namely, \((J_1, J_2)=(4,14)\) and \((8,12)\)—limiting the accuracy with which the dissociation energy can be independently determined. In fact, we can fit all angular distributions (including those associated to excitation of the “bound” \(\nu_2\) HCl stretch) using \(D_0\)’s between 434 and 448 cm\(^{-1}\). In the analysis which follows we simply use the value determined by Ni \textit{et al.}\(^{28}\).

The next step is to fit the experimental angular distributions. For this purpose, we have developed a program that calculates the angular distribution for a specific channel by Monte Carlo averaging over the instrumental geometry. The results of these calculations were then used to fit the experimental angular distribution using a least-squares procedure.
yielding the relative probabilities for the various photofragment channels. The solid line in Fig. 5 shows the result of this fitting procedure for the $v_1^RQ_0(1)$ transition and the vertical bars show the position of maximum intensity and the probability of the photofragment channels. The result of this fit is clearly in good agreement with the experimental results. The “argon-seeded” experimental angular distribution, shown as an inset of Fig. 5, was then calculated using the probabilities fixed at 439 cm$^{-2}$, independent of the specific vibrational excitation within the complex.

Again, the vertical bars indicate the probabilities of the open photofragment channels. With the probabilities fixed, the “argon-seeded” angular distributions are also well reproduced. Note that the angular distributions for both $v_2^R$ sub-bands are quite similar, as is the available energy. Apparently, the additional excitation of $K_a=1$ in the $v_2^R$ HCl stretch does not significantly change the associated dissociation dynamics.

**B. Comparison between calculations and experiments**

The most direct way to compare the result of our calculations with the experimental data is to calculate the angular distributions that results from our computed rotational-state distributions. For the $v_2^R$ state of $B_2^1$ symmetry, the result is shown in Fig. 6(a). The theoretical curve reproduces the experiment quite well, although the second peak is somewhat stronger in the calculation, reflective of the predicted probability for the $(3,14)$ channel being somewhat too high. Given the sensitivity of the distribution to the potential surface, the agreement is actually surprisingly good. Unfortunately, we cannot compare the other experimental angular distributions in this way since they involve the additional excitation of $K=1$ in the vibrational excited state of the HCl dimer, for which no calculations were performed.

There have been three experimental studies by Ni and co-workers$^{28,43,45}$ on the rotational-state distribution of HCl fragments with which we can compare the results presented above. Using position-sensitive translational spectroscopy (POSTS),$^{43}$ they were able to determine a complete quantum-state-resolved distribution of rotational states $J_{HCl}$ $\geq$ 10. In Fig. 8(a) we show a comparison between their distributions$^{28}$ and those obtained from our theoretical and experimental data, by summing over the states of the other fragment: namely, $D(j_2) = \Sigma_{j_1} P(j_1,j_2)$ for the $v_2^R$ band. The $J$ labeling for IR transitions is used in this figure; i.e., the $v_2^R/v_2^L$ transitions probe the upper/lower tunneling states of the dimer. It is clear that the probability distributions are qualitatively consistent with those of Ni and co-workers, although our experimental results suggest a somewhat larger contribution from the highest rotational state $(j_2=14)$. Note that the agreement between the data of Ni and co-workers with our theoretical data is quite good for the $v_2^L$ excitation. For the $v_2^R$ transitions the theoretical distributions underestimate the contributions from the $j_2=12$ and 13 states.

Figure 8(b) shows the distribution for dissociation from a $v_1^R$ excited state. For the $v_1^R$, the calculated probability for the highest rotational state $(j_2=14)$ is clearly too large, while the theoretical distributions underestimate the contributions from the $j_2=12$ and 13 states. For the $v_1^R$ excited state no direct comparison with experiments can be made, but looking at Fig. 8(b), we see that it closely resembles the experimental distribution of its tunneling partner, in fact more so than the calculation for this symmetry.

Ni and co-workers also determined the product correlation for states in which one of the molecules is in rotational state $j_2=14$,$^{43}$ indicating that a major fraction, 86%, was found in (4,14) and 14% in (3,14). The upper limits for the ratio of the remaining $(j_1,14)$ states were estimated to be less...
than 5% for \( j_1 = 2 \) and less than 2% for \( j_1 = 1 \) with essentially no population of the (0,14) channel. Figure 8(c) shows a comparison of their results with the present experimental and theoretical data. Here again we see that the \( \nu_2 \) distribution agrees better with the experimental data [see also Fig. 6(a)] than that of \( \nu_2 \).

Looking in more detail at the dissociation channels individually, we show in Fig. 9 the contributions of the highest dissociation channels to the rotational-state distributions of the \( \nu_2 \) excited state of \( A_1 \) symmetry. It is immediately obvious from Fig. 9 that the computed contributions to the (8,12) and (6,13) channels are much too low when compared with the experimental distribution of Ni et al.\textsuperscript{28} The lack of probability in these two channels is the cause of the low probabilities for \( j_2 = 12 \) and 13 in Fig. 8(a). A further comparison with the experimental data for the \( \nu_1 \) (Ref. 28) is not possible due to an apparent error in the plotting of their correlated probabilities.\textsuperscript{61}

Färnık et al.\textsuperscript{47,62} found two interesting trends for the combined excitation of a monomer stretch mode and the \( \nu_4 \) and \( \nu_5 \) excitations. The first was that all observed transitions were based on the excitation of the donor stretch \( \nu_2 \) and the second that three of the four observed combination bands originated from the upper tunneling level of the ground state. Our full-dimensional calculations of the line strengths for transitions from the \( J = 1, K = 0 \) ground state to \( J = 0 \) predissociating states support both observations; see Table VI. The \( \nu_2 + \nu_4 \) and \( \nu_2 + \nu_5 \) transitions are much stronger than their \( \nu_1 \) counterparts. Also, for these combined excitations, the transitions to the excited states of \( A_1 \) symmetry, which originate from the upper tunneling level of the ground state, clearly dominate.

This last effect is much stronger than in the case of HF dimer,\textsuperscript{42} as was already pointed out by Färnık et al.\textsuperscript{62} They explain this effect in terms of the fact that the tunneling barrier in (HF)\textsubscript{2} is much higher than in the HCl dimer. As a result, the HF dimer wave functions are much more localized in the two wells on the \( \nu_3 \) tunneling path. The difference between \( A_1 \) and \( B_2 \) tunneling states is then much smaller than in HCl dimer, where the \( A_1 \) states have significant amplitude in the region of the barrier, whereas the \( B_2 \) states have a nodal plane in this location.

It is interesting to note that the strongest combination band, according to our calculations, is \( (\nu_2 + \nu_5)^2 \), which was also found to be strongest in the 3D model calculation by Färnık et al. Nevertheless, it was not observed in their experiments, although the computed energy difference (2897...
places it in the region of the spectrum that was investigated.

VII. COMPARISONS BETWEEN THE HCl AND HF DIMERS

In making comparisons between the photodissociation dynamics of HCl and HF dimers it is important to emphasize that the overall trend in the latter system was for the population of “high-j–low-j” exit channels, explained in terms of an impulsive dissociation from equilibrium geometry resulting in high/low rotational excitation of the proton donor/acceptor fragments. In addition, states with low recoil energies were preferred over those with high translational energies. The experimental results for HCl dimer presented here are also highly nonstatistical, again showing preference for channels with low recoil energies. On the other hand, the similar probabilities for the (4,14) and (8,12) channels suggest a lack of clear “high-j–low-j” exit channels, as also illustrated by a low probability for other (j,14) channels. This is consistent with the floppier nature of the HCl dimer, which makes the asymmetric proton-donor/proton-acceptor geometry less important than for HF dimer.

VIII. CONCLUSION

We have studied the vibrational predissociation of HCl dimer using both theory and experiment. All of the experimental results presented here are consistent with the dissociation energy of 439 cm$^{-1}$ reported by Ni et al.\textsuperscript{28} Furthermore, we find that the polarization of the laser does not have an effect on the observed angular distributions, in contrast with earlier observations on the HF dimer. We attribute this effect to the nuclear hyperfine depolarization in the case of (HCl)$_2$.

Calculations based upon the ES1–EL potential energy surface give linewidths that are 1–2 orders of magnitude smaller than experiment. The rotational-state distributions agree reasonably well with experimental data, although the computed distributions for scattering states of even permutation symmetry are systematically further from the experimental results. Given that the distributions are converged with respect to the angular basis, we suspect that this is a problem with the potential energy surface. Since the lifetime depends upon the coupling between the intramolecular and intermolecular coordinates in the small-R region of the potential, the implication is that the coupling is too weak. As was mentioned previously, there is other evidence that this coupling is also too weak in the ES1 potential. The ES1–EL potential was corrected by adding an $r_A$, $r_B$-dependent dipole–dipole interaction term, which is inherently long range. Hence the disagreement between calculated and measured linewidths can most likely be attributed to the fact that this correction term is only an estimate of the coupling. On the other hand, the rotational-state distributions are more dependent on the anisotropy of the ground-state potential. The fact that the ES1 potential is fit to spectroscopic data that directly probes this anisotropy suggests that the relevant interactions are faithfully reproduced. As a result, the rotational-state distributions are in better agreement with the experimental data than the linewidths. In comparison with the dissociation dynamics of the HF dimer, we find that HCl “high-j–low-j” exit channels are less dominant in the angular photofragment distributions. This is consistent with the floppier HCl dimer structure, which makes the two HCl subunits less distinguishable than in the equilibrium proton-donor/proton-acceptor geometry.

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\begin{thebibliography}{10}
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61. J. J. Valentini (private communication).