Low frequency vibrational anharmonicity and nuclear spin effects of Cl\(^{−}\)(H\(_2\)) and Cl\(^{−}\)(D\(_2\))

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Low frequency combination bands of \(^{35}\)Cl\(^{−}\)(H\(_2\)) and \(^{35}\)Cl\(^{−}\)(D\(_2\)) have been measured in the region between 600 and 1100 cm\(^{−}\)\(^{1}\) by infrared predissociation spectroscopy in a cryogenic 22-pole ion trap using a free electron laser at the FELIX Laboratory as a tunable light source. The \(^{35}\)Cl\(^{−}\)(H\(_2\))\((^{35}\)Cl\(^{−}\)(D\(_2\))) spectrum contains three bands at 773 cm\(^{−}\)\(^{1}\) (620 cm\(^{−}\)\(^{1}\)), 889 cm\(^{−}\)\(^{1}\) (692 cm\(^{−}\)\(^{1}\)), and 978 cm\(^{−}\)\(^{1}\) (750 cm\(^{−}\)\(^{1}\)) with decreasing intensity toward higher photon energies. Comparison of the experimentally determined transition frequencies with anharmonic vibrational self-consistent field and vibrational configuration interaction calculations suggests the assignment of the combination bands \(v_1 + v_2, 2v_1 + v_2, \) and \(3v_1 + v_2\) for \(^{35}\)Cl\(^{−}\)(H\(_2\)) and \(2v_1 + v_2, 3v_1 + v_2, \) and \(4v_1 + v_2\) for \(^{35}\)Cl\(^{−}\)(D\(_2\)), where \(v_1\) is the \(^{35}\)Cl–H\(_2\) stretching fundamental and \(v_2\) is the Cl–(H\(_2\)) bend. The observed asymmetric temperature dependent line shape of the \(v_1 + v_2\) transition can be modeled by a series of \(\Sigma^+\) ro-vibrational transitions, when substantially decreasing the rotational constant in the vibrationally excited state by 35%. The spectrum of \(^{35}\)Cl\(^{−}\)(D\(_2\)) shows a splitting of 7 cm\(^{−}\)\(^{1}\) for the strongest band which can be attributed to the tunneling of the ortho/para states of D\(_2\).

I. INTRODUCTION

Spectroscopic studies of dihydrogen halide anions X\(^{−}\)(H\(_2\)) with (X = F, Cl, Br, I) in the gas phase reveal rich dynamical processes of benchmark chemical reactions. Photoelectron spectroscopy of F\(^{−}\)(H\(_2\)) has shown the importance of vibrational bending modes to reactive scattering resonances in the prototypical F + H\(_2\) reaction forming HF + H.\(^{1−3}\) Vibrational predissociation spectroscopy by resonant driving of the H\(_2\) stretch fundamental has been used to reveal the linear structure and to explore the potential energy surface (PES) of the anionic halide complexes.\(^{4−8}\) However, direct spectroscopic observation of the low-lying bending vibrations, which correspond to hindered H\(_2\) rotation, and the dissociative X–H\(_2\) stretching vibrations has not been reported yet.

Probing the transition state dynamics relies on an accurate knowledge of the PES for the closed shell anionic complex. Substantial work has been carried out to compute and characterize the PES of halide complexes.\(^{9−13}\) The long-range interactions of the Cl\((H_2/D_2)\) potential is in good agreement with direct probing of vibrationally excited states by predissociation spectra highly above the vibrational ground state.\(^{7}\)

Anionic dihydrogen halide complexes X\(^{−}\)(H\(_2\)) are weakly bound complexes based on electrostatic ion-quadrupole (α R\(^{−}\)) or ion-induced dipole interactions (α R\(^{−}\)). Typical dissociation energies range from D\(_0\) = 1573 cm\(^{−}\)\(^{1}\) at an equilibrium bond length of R\(_e\) = 1.74 Å for F\(^{−}\)(H\(_2\)) to D\(_0\) = 253 cm\(^{−}\)\(^{1}\) and R\(_e\) = 3.76 Å for I\(^{−}\)(H\(_2\)).\(^{5,12}\) These complexes are similar to the dihydrogen hydride anion H\(_3\)\(^{−}\), which also features a collinear structure of C\(_{\text{inv}}\) symmetry with a binding energy of D\(_0\) = 401 cm\(^{−}\)\(^{1}\).\(^{14}\) H\(_3\)\(^{−}\) is discussed as a possible tracer for H\(^{−}\) anions in interstellar molecular clouds\(^{15}\) and is also a benchmark system for anion-neutral reactions.\(^{16−18}\) However, direct spectroscopic studies of this system are still elusive.

Two experimental consequences of the weak binding energy and the large internuclear separation of the X–H\(_2\) complexes arise. On the one hand, the fundamental X–H stretch vibration and the large amplitude bending motion are expected to be in the mid-IR region below 1000 cm\(^{−}\)\(^{1}\). And, on the other hand for spectroscopic investigations with sufficient photon interaction times, the complexes have to be formed and stabilized in a cryogenic environment.

Here, we report results on the strongly anharmonic vibrational structure of low frequency modes in Cl\(^{−}\)(H\(_2\)) and Cl\(^{−}\)(D\(_2\))
probed by single photon infrared predissociation (IRPD) spectroscopy. We used a cryogenic 22-pole ion trap that offers an environment in which the complexes can be efficiently formed from trapped anionic halides via a ternary inelastic collision (attachment process) with $\text{H}_2/\text{D}_2$ buffer gas. The necessity of a wide tunability in the mid-IR region at high photon flux asks for solutions beyond commercially available table top laser systems. We therefore used the FELIX laser facility as the light source. Below we present infrared predissociation spectra in the region of 600 to 1100 cm$^{-1}$ and compare our results to the calculated \textit{ab initio} anharmonic vibrational spectra. For that, we applied the Vibrational Self-Consistent Field and Configuration Interaction (VSCF/VCI) approach, which is capable of capturing overtones and combination bands by inclusion of mode-coupling.

II. METHODS

A. Experimental methods

The experiments were carried out at the cryogenic 22-pole trap instrument FELion which is a user end station at the Free Electron Laser for Infrared eXperiments (FELIX) at Radboud University, Nijmegen. Chlorine anions were produced in an ion storage source by dissociative electron attachment to $\text{CCl}_2\text{F}_2$. The ions were extracted in a pulsed scheme, and $^{35}\text{Cl}^-$ ions were mass selected by using a quadrupole mass filter. Typically around 50 000 anions were trapped in a cryogenic 22-pole ion trap at variable temperatures between 8 and 22 K. Halide anion complexes with hydrogen were formed after insertion of a dense $\text{H}_2$ seeded in a $\text{He}$ buffer gas pulse (number densities of $> 10^{14}$ cm$^{-3}$). About 5000 complexes were formed on average per trap filling. Both the buffer gas and thereby the ions are assumed to thermally equilibrate on short time scales with the temperature of the trap walls which guarantees that the ions are prepared in the vibrational ground state. The complexes were stored for 2-3 s, while the pulsed laser beam irradiated the trapped complexes.

FELIX FEL 2 was used for IRPD measurements in the 300-1200 cm$^{-1}$ frequency range, delivering up to 30 mJ in a few microsecond long pulses at a repetition rate of 10 Hz. A second quadrupole mass filter transmits the complex of interest to an MCP detector. The laser induced parent depletion signal $N$ was recorded as a function of photon energy with a step size of 1 cm$^{-1}$. The obtained vibrational predissociation spectra were background $N_0$ and laser fluence $f$ normalized to the ion loss $s = -\ln(N/N_0)^{1/f}$. Three to eight scans for one trap temperature were averaged, and finally a running average of over 3 data points was applied to produce the spectra presented here.

B. Computational methods

In order to obtain the calculated anharmonic vibrational spectrum, the initial $^{35}\text{Cl}^-(\text{H}_2)$ geometry was optimized at the explicitly correlated coupled-cluster level of theory (CCSD(T)-F12) using basis sets of triple-zeta quality (cc-pVTZ-F12). The vibrational spectra were calculated solving the nuclear Schrödinger equation with the Vibrational Self-Consistent Field (VSCF) approach. This approach takes anharmonicities and mode-mode coupling into account and enables the calculation of combination bands and overtones.

A prerequisite is the computation of a high-quality Potential Energy Surface (PES). In a first step, the normal mode harmonic oscillator approximation was employed to obtain normal modes $q_i$ as coordinates for the subsequent PES generation. The harmonic oscillator approximation also yields the harmonic vibrational energies and the zero-point energy (ZPE). With the normal modes $q_i$ as coordinates, a multimode representation of the Potential Energy Surface (PES) was

![FIG. 1. Top: the normal modes of the linear system $^{35}\text{Cl}^-(\text{H}_2)$ denoted as dissociation $q_1$, bend $q_2$, and stretch $q_3$ are depicted together with the one-mode potentials. Bottom: The two-mode potentials are shown. All potentials are computed at the CCSD(T)-F12/cc-pVTZ-F12 level of theory.]
generated on a grid with CCSD(T)-F12/cc-pVTZ-F12 single points and transformed to a polynomial representation, using the implemented methods by Rauhut et al.\textsuperscript{24,25}

In Fig. 1, the normal modes \( q_i \) are depicted together with one-mode and two-mode potentials. The one-mode potentials \( V(q_1) \) and \( V(q_3) \) are similar to a Morse potential, whereas \( V(q_2) \) resembles a quartic potential. The PES is rather local, as can be seen for the two-mode potentials, where the periphery is energetically not balanced. With the polynomial representation of the PES, the time-independent nuclear Schrödinger equation is solved variationally by the VSCF approach and correlation-corrected by the configuration-selective state-specific Vibrational Configuration Interaction (VCI).\textsuperscript{26} This yields the anharmonic vibrational energies and the anharmonic zero point energy (AZPE).

Bond Dissociation Energies (BDEs or \( D_0 \)) were calculated with CCSD(T)-F12/cc-pVTZ-F12. For the harmonic BDEs, all ZPE comes from the harmonic approximation. In the case of anharmonic BDEs, the ZPE of the \( \text{H}_2 \) and \( \text{Cl}^- \) species was from the harmonic approximation, whereas the ZPE of the tri-atomic complex, e.g., \( \text{Cl}^- \cdot \text{H}_2 \), corresponds to the VCI ground state energy. In order to compute isotopic shifts, the whole procedure of PES generation and VSCF/VCI calculation is repeated with the mono-isotopic mass of deuterium. Calculations were performed with the MOLPRO software package.\textsuperscript{27}

The anharmonic infrared intensities, both in the VSCF and the VCI calculations, are based on a multi-mode representation of the dipole surface, which is generated on a grid (with energy gradients at the HF/cc-VTZ-F12 level of theory) and then transformed into a polynomial representation, analogous to the PES generation mentioned above.

### III. RESULTS AND DISCUSSION

#### A. Combination bands of \( \text{Cl}^- \cdot \text{H}_2 \)

Figure 2 shows the single photon vibrational predissociation spectrum of \(^{35}\text{Cl}^- \cdot \text{H}_2\) at 8 K trap temperature in the photon energy range of 600 to 1200 cm\(^{-1}\). Three vibrational bands at 773 cm\(^{-1}\), 889 cm\(^{-1}\), and 978 cm\(^{-1}\) were found. No additional features were found in searches up to 1700 cm\(^{-1}\). The bands show an asymmetric shoulder toward lower photon energies and drop in intensity by 70% from the first to second band and 40% from the second to third band. The spectral region from 300 to 600 cm\(^{-1}\) was scanned, but no additional vibrational features were found.

In the normal mode picture, the linear system of \( \text{C}_{\text{ov}} \) symmetry possesses the \( \text{Cl}^- \cdot \text{H} \) stretching mode (\( q_1 \)) which is the dissociative channel, the doubly degenerate \( \text{Cl}^- \cdot \text{H}_2 \) bending (\( q_2 \)), and the dipole allowed \( \text{H}_2 \) stretching (\( q_3 \)) vibration. For the three modes, the harmonic approximation (CCSD(T)/cc-pVTZ-F12) yields fundamental vibrational transitions of \( v_1 = 216 \text{ cm}^{-1} \), \( v_2 = 520 \text{ cm}^{-1} \), and \( v_3 = 4218 \text{ cm}^{-1} \) (see Table I). Anharmonic calculations yield \( v_1 = 206 \text{ cm}^{-1} \), \( v_2 = 578 \text{ cm}^{-1} \), and \( v_3 = 4016 \text{ cm}^{-1} \) for the fundamental transitions. Compared to a harmonic potential, mainly the inclusion of mode-coupling causes a red shift of 5% for \( v_1 \) and \( v_3 \). In the case of the large amplitude bending transition, the quartic potential causes a blue shift of 11% for the fundamental transition compared to harmonic calculations. Clearly, the experimentally observed features cannot be explained by these vibrational bands.

The anharmonic dissociation energy of the complex is calculated to be \( D_0 = 324 \text{ cm}^{-1} \) (CCSD(T)-F12/cc-pVTZ-12). Transitions below the dissociation threshold cannot be observed in a single photon predissociation scheme, which prohibits the detection of the only bound state \( v_1 \) within the potential. Anharmonic calculations suggest the intensity of the fundamental \( v_2 \) transition (about 1.3 km/mol) to be one to two orders of magnitude weaker than the intensities of \( v_1 \) (about 9 km/mol) and \( v_3 \) (about 145 km/mol). This can explain the absence of this vibration, which is the only fundamental vibrational band within our measured spectrum.

The most plausible explanation of the observed bands is combinations of \( v_2 \) fundamental excitations with the fundamental of \( v_1 \) or its overtones. Pure overtones of \( v_1 \) can be excluded as the measured bands lie in the dissociation continuum of the \( \text{Cl}^- \cdot \cdot \cdot \text{H}_2 \) stretching excitation. Combining the calculated anharmonic fundamental frequencies suggests transition frequencies at \( v_1 + v_2 = 784 \text{ cm}^{-1} \), \( 2v_1 + v_2 = 990 \text{ cm}^{-1} \),

![FIG. 2. Vibrational predissociation spectrum of \(^{35}\text{Cl}^- \cdot \text{H}_2\) at 8 K trap temperature. The upper spectrum was taken with normal \( \text{H}_2 \), having an ortho to para ratio of 3:1. The lower spectrum was taken with a \( \text{H}_2 \) mixture of an ortho to para ratio of 1:99.](image-url)
and $3v_1 + v_2 = 1196 \text{ cm}^{-1}$. The first combination agrees well with the strongest measured band, which suggests its assignment to the (1,1,0) band. The other estimates are more widely spaced than the measured bands. In the absence of other possible vibrational combinations, this is evidence for strong anharmonic red-shifting of the $v_1$ overtones. Thus, we attribute the second and third observed bands to the (2,1,0) and (3,1,0) bands.

To test this assignment, we compare the measured bands to the VSCF/VCI calculations of the harmonic and anharmonic fundamental and combination band positions of $^{35}\text{Cl}\cdotp (\text{H}_2)$ (see Table I). The H$_2$ stretch fundamental with a calculated band origin of 4016 cm$^{-1}$, which becomes dipole allowed due to the interaction with Cl$^-$, agrees with only 0.3% deviation with the measurements of Wild et al.$^7$ The VCI calculations confirm the assignment of the three low frequency vibrations to be $v_1 + v_2$, $2v_1 + v_2$, and $3v_1 + v_2$ with a deviation from the experimentally found values of 0.6%, 3.4%, and 0.4%, respectively. These differences are expected to mainly reflect the overall numerical stability of the VCI calculation, which is estimated to yield band positions with an accuracy of not better than within 20 cm$^{-1}$.

The fact that combination bands are observable, while the $v_2$ fundamental is not, is assumed to occur by a transfer of intensity from the fundamental $v_1$ into the combination bands (n,1,0) as found previously for ArHF.$^{28}$ We expect that higher overtones of $v_1$ in combination with $v_2$ were not observed because of decreasing absorption intensities for higher overtones.

We additionally performed measurements on $^{35}\text{Cl}\cdotp (p\text{-H}_2)$ with para-H$_2$. A 11 PTFE coated para-H$_2$ bottle with an approximate ortho-para ratio of $10^{-4}$ was prepared in Cologne and used at the FELion setup 27 h later with an approximate ortho-para ratio of $10^{-2}$. The IRPD spectrum of $^{35}\text{Cl}\cdotp (p\text{-H}_2)$ included in Fig. 2 shows no significant difference to normal H$_2$, containing a 3:1 ratio of ortho to para. This may be caused by remaining 1% of o-H$_2$ in the reservoir and an efficient switching from para to ortho in the anion complex.$^7$ (see also Sec. III D).

### B. Transition line shapes of $^{35}\text{Cl}\cdotp (\text{H}_2)$

Figure 3 shows the strongest band of $^{35}\text{Cl}\cdotp (\text{H}_2)$ at (a) 8 K and (b) 22 K trap temperature in blue. The line profile of both measurements clearly shows an asymmetry toward lower photon energies. The full width at half maximum (FWHM) linewidth of the 8 K band is 4.3 cm$^{-1}$ while at 22 K it amounts to 7.6 cm$^{-1}$. The typical FWHM linewidth of FELIX lies between 3.6 and 5.4 cm$^{-1}$ (0.2% and 0.3% rms), thus, a clear broadening beyond the FEL linewidth is observed.

According to the VSCF/VCI calculations, all observed transitions are from a linear structure of the vibrational ground state with $\Sigma^+$ symmetry into an excited bending vibrational state with $\Pi$ symmetry. Therefore the rovibrational spectrum has to include a Q-branch. The measured rotational constant of the complex in the vibrational ground state is $B_0 = 0.9207 \text{ cm}^{-1}$ and, thus, too small to obtain rotationally resolved spectra at the given FELIX linewidth.

A convolution of the FELIX linewidth with simulated rovibrational transitions was fitted to the predissociation spectrum of the $v_1 + v_2$ transition by using PGopher$^{29}$ (see Fig. 3 and Figs. S1 and S2). When including an assumed predissociation lifetime broadening of about 1 cm$^{-1}$ in the convolution, we found that the measured line shape could only be fitted with a rotational temperature much lower than the actual trap temperature. This shows that lifetime broadening has to be smaller and cannot be resolved, given the linewidth of the FELIX laser. In the final fit, the rotational state population was set to the nominal trap temperature of 8 and 22 K. The vibrational ground state constants $B_0 = 0.9207 \text{ cm}^{-1}$ and $D_0 = 9 \times 10^{-5} \text{ cm}^{-1}$ were taken from Ref. 7. The best agreement with the experimental findings requires a substantial decrease in the rotational constant $B' = 0.6 \text{ cm}^{-1}$ and an increase in the centrifugal distortion constant $D' = 1 \times 10^{-3} \text{ cm}^{-1}$ in the vibrationally excited.

### Table I. VSCF/VCI calculated dissociation energies $D_0$, calculated harmonic and anharmonic (VCI/CCSD(T)-F12/cc-pVTZ-F12) transition frequencies, and experimentally found band positions for both isotopes $^{35}\text{Cl}\cdotp (\text{H}_2)$ and $^{35}\text{Cl}\cdotp (\text{D}_2)$ in cm$^{-1}$. The top three rows show the anharmonic fundamental modes. The bottom three rows show the combination bands.

| Transition | Calculation harmonic | Anharmonic | Experiment |
|------------|---------------------|------------|------------|
| $D_0$      | 365$^a$             | 324        | ...        |
| (1, 0, 0)  | 216                 | 206        | ...        |
| (0, 1, 0)  | 520                 | 578        | ...        |
| (0, 0, 1)  | 4218                | 4016       | 4005$^b$   |
| (2, 0, 0)  | ...                 | 342        | ...        |
| (3, 0, 0)  | ...                 | 466        | ...        |
| (4, 0, 0)  | ...                 | 603        | ...        |
| (1, 1, 0)  | ...                 | 777        | 773        |
| (2, 1, 0)  | ...                 | 860        | 889        |
| (3, 1, 0)  | ...                 | 982        | 978        |
| (4, 1, 0)  | ...                 | 1135       | ...        |

$^a$CCSD(T)-F12/cc-pVTZ-F12  
$^b$Wild et al.$^7$
state. Thus, the vibrationally averaged $^{35}\text{Cl}^{-}(\text{H}_2)$ distance of the complex increases by 19% from 3.06 Å to 3.79 Å. A similar behavior has been reported by Lovejoy et al. for the ArHF van der Waals complex. There, the vibrationally averaged complex size changes from 3.13 Å in the vibrational ground state to 4.6 Å upon excitation of the second overtone of the Ar-HF stretch fundamental in combination with the fundamental HF stretch.

An alternative mechanism that could result in an effective asymmetric broadening of the observed bands is l-type doubling, where the degeneracy of the $\Pi$-type $v_2$ transition is lifted upon end-over-end rotation of the complex. We have estimated this by computing the rotational l-type doubling constant, which gives the energy difference between $\Pi^+$ and $\Pi^-$ states, using Gaussian09 (CCSD(T)/aug-cc-pVQZ).\textsuperscript{30} We have obtained $q_l < 0.004$ cm\textsuperscript{-1} for rotational excitations up to $J = 10$ (the highest relevant excited rotational state at 22 K). If the employed model of a rigid rotor is a good approximation, this indicates that l-type doubling is too small to have any effect on the measured line shape.

C. Combination bands of Cl$^{-}$(D$_2$)

In order to investigate the isotopic shifts of the Cl$^{-}$(H$_2$) complex, the deuterated species was spectroscopically investigated in the range of 500 to 1000 cm\textsuperscript{-1}. Figure 4 shows the predissociation spectrum of $^{35}\text{Cl}^{-}(\text{D}_2)$ at 22 K trap temperature. Three bands centered around 620 cm\textsuperscript{-1}, 692 cm\textsuperscript{-1}, and 750 cm\textsuperscript{-1} were observed. Two bands show a clear splitting, while for the third band, the splitting is not resolved; this splitting is discussed in Sec. III D.

Table I shows the measured and calculated transition frequencies and dissociation energy for $^{35}\text{Cl}^{-}(\text{D}_2)$. In contrast to the hydrogenated complex, the number of bound states of $^{35}\text{Cl}^{-}(\text{D}_2)$ is significantly larger. Our calculations show for $v_1 = 134$ cm\textsuperscript{-1} that the third overtone $4v_1 = 464$ cm\textsuperscript{-1} as well as the fundamental $v_2 = 382$ cm\textsuperscript{-1} transition still lies below the calculated dissociation threshold of $D_0 = 525$ cm\textsuperscript{-1}. Also the (1,1,0) transition in $^{35}\text{Cl}^{-}(\text{D}_2)$, calculated to be at 491 cm\textsuperscript{-1} (CCSD(T)-F12/VTZ-F12), is below the dissociation energy and thereby not expected to be observed in single photon absorption. The experimentally observed bands are assigned to the (2,1,0), (3,1,0), and (4,1,0) bands. The first two are shifted by a factor of 0.69 and 0.71 with respect to the non-deuterated complex, which agrees well with the expected $2^{-1/2}$ scaling. The deviation between the experiment and calculations is within 6% for (2, 1, 0) and 1.5% for (3, 1, 0). The (4,1,0) band position is substantially overestimated by the anharmonic calculation.
D. Tunneling splitting in Cl−(D2)

Upon deuteration, the strongest band of 35Cl−(D2) at 620 cm−1 splits into two bands separated by about 7 cm−1. This can be explained by a splitting of the vibrational states due to tunneling through the barrier for hindered rotation of the D2 unit. For free deuterium molecules, the difference in rotational ground state energy between J = 0 (ortho-D2) and J = 1 (para-D2) is about 60 cm−1. Accordingly, for an unhindered internal rotation of D2 within the anionic complex, a splitting of 60 cm−1 would be observed. For an infinite barrier for internal rotation, both species would be degenerated and thereby indistinguishable in the spectrum. The observed splitting of 7 cm−1 can be explained by the difference of the tunneling splittings for the ground and excited vibrational states. This difference is actually expected to be dominated by the tunneling splitting in the excited state because this state is closer to the classical barrier for the hindered rotation. Permutation symmetry requires that one of the two eigenstates caused by the tunneling of the hindered rotor corresponds to para-D2 and the other to ortho-D2.

For the case of 35Cl−(H2), an even larger tunneling splitting than for 35Cl−(D2) may be expected. However, no splitting is observed in the 35Cl−(H2) spectrum (see Sec. III B). This is explained by the absence or strong suppression of Cl−(p-H2) complexes in the trap. By comparing the predissociation spectra of 35Cl(H2) to 35Cl(D2) upon excitation of the H2/D2 stretching fundamental, Wild et al. found an efficient exothermic ligand switching from para-H2 to ortho-H2. This switching, which is driven by the weaker interaction between Cl− and p-H2 due to the absence of a quadrupole moment and the 120 cm−1 higher binding energy of the o-H2 complex, is expected to take place in our ion trap as well.

In the case of D2, the ligand switching to the more strongly bound para state is less efficient than that for H2. The reason is that the interaction strength is reversed, the quadrupole moment exists for the more weakly bound ortho state, and the binding energy difference is a factor of two smaller. Thus, both ortho- and para-D2 complexes can be expected to exist in the ion trap. This is in line with Wild’s study, who found that an increase in the quadrupole moment of para-D2 upon vibrational excitation of the D2 stretching vibration caused a tunneling splitting. In the case of 35Cl−(D2), they observed a splitting of 0.24 cm−1 in the v3 stretching fundamental, which was lacking in the 35Cl−(H2) data.

The two individual bands of the (2, 1, 0) band of 35Cl−(D2), taken at 22 K, show a FWHM of 2.8 cm−1 (blue-shifted peak) and 4.9 cm−1 (red-shifted peak) (see Fig. 4), significantly lower than the 7.6 cm−1 FWHM linewidth of the 22 K (1, 1, 0) band of the 35Cl−(H2) spectrum. Upon cooling the trap from 22 K to 8 K, the width of these bands remains roughly unchanged (Fig. 4, inset). Given the FELIX linewidth in this spectral range of about 3 cm−1 (FWHM), it seems that the blue-shifted band is composed of transitions from only very few rotational states, in contrast to the red-shifted band. To explain this, a quantitative simulation of the band shapes is required which also takes into account the tunneling splitting and the ortho and para hyperfine states. We hope that our work stimulates further theoretical calculations toward this goal.

IV. CONCLUSION

Infrared predissociation spectroscopy in a cryogenic 22-pole trap using FELIX as a tunable light source was performed on Cl−(H2) in the frequency range of 300–1200 cm−1. Three bands were found at 773 cm−1, 889 cm−1, and 978 cm−1. By anharmonic VSCF/VCI calculations, the bands are assigned to the combination bands v1 + v2, 2v1 + v2, and 3v1 + v2, respectively.

A temperature dependent analysis of the v1 + v2 band shape shows broadening when increasing the trap temperature from 8 to 22 K. Although individual rotational lines cannot be resolved, the overall band shape indicates a substantial increase in the complex size, i.e., the Cl−···H2 distance, upon excitation of a transition involving a stretching mode. In line with findings on the H2 stretch fundamental, no evidence for the formation of the para-H2 complex was found.
temperatures of the \(v_1\) transition band of \(\text{Cl}_2\).

To address the influence of the zero point energy, \(\text{Cl}^- (\text{D}_2)\) was studied. Again three bands were found at 620 cm\(^{-1}\), 692 cm\(^{-1}\), and 750 cm\(^{-1}\). The two lower bands show a tunneling splitting of 7 cm\(^{-1}\) which is attributed to the ortho- and para-\(\text{D}_2\) nuclear spin isomers of the \(\text{Cl}^- (\text{D}_2)\) complex.

Our study on low frequency vibrations provides data to test the potential energy surface close to the dissociation threshold. Specifically, improving the reliability of the anharmonic energies in VCI calculations requires a CI space that is not provided by the present PES, which has been computed relatively locally around the equilibrium geometry. Further investigations incorporating a global PES are desirable to improve the accuracy of the calculations. Furthermore, more sophisticated models are needed to explicitly treat the tunneling splitting of the ortho and para states and the resonance character of the excited vibrational states due to their coupling to continuum states.

**SUPPLEMENTARY MATERIAL**

See supplementary material for fitting results for different rotational constants and transition types at two different temperatures of the \(v_1 + v_2\) transition band of \(\text{Cl}^- (\text{H}_2)\).

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