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Photoelectron spectroscopy of ClH_2^- and ClD_2^- : A probe of the $\text{Cl}+\text{H}_2$ van der Waals well and spin-orbit excited states

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Photoelectron (PE) spectra of ClH_2^- and ClD_2^- were measured at 299 nm (4.154 eV). Photodetachment of these anions accesses the prereactive van der Waals well on the ground state $\text{Cl}+\text{H}_2$ potential energy surface, as well as the low-lying spin-orbit excited states resulting from the interaction of Cl and Cl^* with H_2 . The PE spectra are dominated by two relatively narrow peaks corresponding to transitions to the neutral $\text{Cl}\cdot\text{H}_2$ and $\text{Cl}^*\cdot\text{H}_2$ complexes. The energetics and widths of these features are interpreted in terms of the properties of the anion and neutral potential energy surfaces. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518998]

Recent experimental and theoretical studies have shown the “simplest Cl reaction,”¹ $\text{Cl}+\text{H}_2\rightarrow\text{HCl}+\text{H}$, exhibits qualitatively new and complex features that raise fundamental issues in our understanding of chemical reaction dynamics. A combined theoretical and experimental study by Skouteris *et al.*² on the $\text{Cl}+\text{HD}$ reaction showed that the presence of a shallow (0.51 kcal/mol) van der Waals (vdW) well in the entrance valley was necessary to reproduce the experimental $\text{HCl}:\text{DCI}$ product branching ratio as a function of collision energy, providing the first experimental evidence that such a well has a measurable effect on a chemical reaction. In addition, there is considerable controversy regarding the reactivity of the spin-orbit excited $\text{Cl}^*(^2P_{1/2})$ state. Experiments by Liu³ indicate that the $\text{Cl}^*(^2P_{1/2})+\text{H}_2$ reaction cross section is comparable or greater than that for $\text{Cl}(^2P_{3/2})+\text{H}_2$, while multisurface reactive scattering calculations by Alexander *et al.*⁴ predict that the reactivity of Cl^* is much smaller than that of Cl . In this Communication, we report the photoelectron (PE) spectrum of the ClH_2^- and ClD_2^- anions, an experiment that directly probes the neutral reactant van der Waals well as well as the Cl spin-orbit structure in the reactant valley.

The results presented here represent a new application of anion PE spectroscopy to reaction dynamics. Previously, we have used negative ion PE spectroscopy to probe the transition state region of several bimolecular reactions.⁵ This “transition state spectroscopy” experiment requires good Franck-Condon overlap between the anion ground vibrational state and the neutral transition state. As an example, the geometry of the FH_2^- anion,⁶ which is essentially F^- clustered to H_2 , is close to that of the relatively “early” barrier for the exothermic $\text{F}+\text{H}_2$ reaction.⁷ The FH_2^- PE spectrum⁸ then yields resolved vibrational structure characteristic of the neutral transition state. In contrast, the slightly endothermic $\text{Cl}+\text{H}_2$ reaction has a much later barrier. Based on the rotationally resolved IR spectrum of ClH_2^- by Bieske^{9,10} and electronic structure calculations of the $\text{Cl}+\text{H}_2$ surface,¹¹ photodetachment of ClH_2^- should have poor overlap with the transition state but excellent overlap with

the van der Waals well in the $\text{Cl}+\text{H}_2$ reactant valley, as shown in Fig. 1. Hence, the PE spectrum of ClH_2^- should directly probe the reactant van der Waals well. In addition, we have shown that negative ion photodetachment of rare-gas halide complexes such as ArCl^- (Ref. 12) reveal how the spin-orbit levels of a free Cl atom are perturbed in the weakly bound ArCl open-shell complex. The PE spectrum of ClH_2^- should yield analogous information for the neutral ClH_2 complex, providing some insight into the controversy regarding Cl^* reactivity.

The photoelectron spectrometer on which these experiments were performed has been described previously.¹³ Briefly, negative ions are generated by crossing a pulsed molecular beam of the appropriate gas mixture with a 1 keV electron beam just downstream of the nozzle. To make ClH_2^- and ClD_2^- , a mixture of 50% H_2 or D_2 in Ar was passed over CCl_4 en route to the pulsed (piezoelectric) valve. The backing pressure was 70 psig, the nozzle diameter was 0.1 mm, and the valve was operated at a repetition rate of 20 Hz. The pulsed beam passes through a skimmer into a differentially pumped region, and negative ions are extracted from the beam by pulsed electric fields and injected into a linear reflectron time-of-flight mass spectrometer with a mass resolution $m/\Delta m\cong 2000$. Mass-selected anions are photodetached at the spatial focus of the mass spectrometer by a pulsed laser at a wavelength of 299 nm (4.154 eV), generated by Stokes-shifting the fourth harmonic (266 nm) of a Nd:YAG laser in a high pressure H_2 Raman cell. PE spectra for ClH_2^- were taken at $m/e=39$ to eliminate background from $^{37}\text{Cl}^-$ at the same mass as $^{35}\text{ClH}_2^-$, while ClD_2^- PE spectra were taken at $m/e=41$. Photoelectrons were collected at the end of a 1 m long, field-free flight tube and energy analyzed by time-of-flight; the energy resolution is 8–10 meV for the spectra shown here. The spectra were taken at a laser polarization angle of 0° with respect to the direction of electron detection; spectra at 90° were similar but much lower in intensity.

Figure 2 shows the PE spectra for ClH_2^- (top) and ClD_2^-

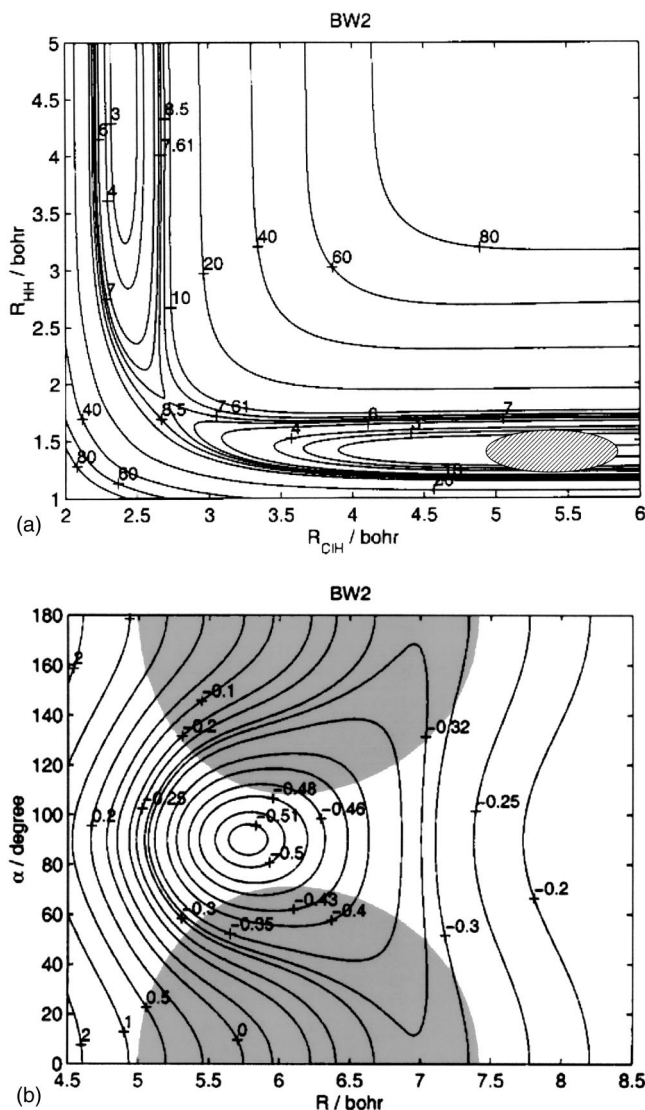


FIG. 1. ClH_2^- equilibrium geometry and ground state wave function (from Ref. 14) superimposed on $\text{Cl}+\text{H}_2$ potential energy surface from Ref. 11. (a) shows a collinear cut through the entrance valley, transition state and exit valley of this surface, while (b) shows the reactant van der Waals well. The values of the contour lines on the potential energy surfaces are in kcal/mol relative to the $\text{Cl}+\text{H}_2$ asymptote.

(bottom). The spectra are plotted as a function of electron binding energy (eBE) given by

$$e\text{BE} = h\nu - e\text{KE}, \quad (1)$$

where $h\nu = 4.154$ eV is the photon energy and $e\text{KE}$ is the measured electron kinetic energy. Each spectrum is dominated by two peaks labeled A(A') and B(B') in the ClH_2^- (ClD_2^-) spectrum. The small peaks at 3.613 eV in both spectra are from Cl^- that is presumably produced by photodissociation of the cluster followed by photodetachment. The small peak between A and B at 3.75 eV in the ClH_2^- spectrum is from $^{35}\text{Cl}(\text{H}_2)_2^-$ at the same mass; this was confirmed by measuring the PE spectrum of $^{37}\text{Cl}(\text{H}_2)_2^-$ at $m/e = 41$. The maxima of peaks A and B occur at 3.683 and 3.793 eV, respectively, with peak widths (FWHM) of 26 and 23 meV. Peaks A' and B' in the ClD_2^- spectra are centered at 3.697 and 3.806 eV, respectively, and have FWHM widths of 52

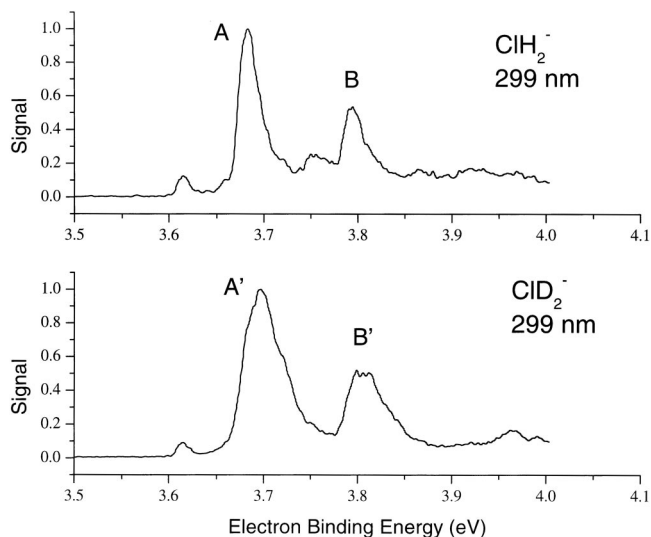


FIG. 2. Photoelectron spectra of ClH_2^- (top) and ClD_2^- (bottom) at 299 nm (4.154 eV). The laser polarization angle was 0° .

and 40 meV, respectively. The onsets of peaks A and A' are at essentially the same energy, 3.666 eV, as are the onsets for peaks B and B' (3.778 eV). In addition, the maximum of peak A coincides with a shoulder on the rising edge of peak A'.

The spacings between the maxima of peaks A and B, 0.111 eV, and peaks A' and B', 0.109 eV, are identical to the Cl spin-orbit splitting of 0.109 eV within our experimental resolution. We therefore assign peaks A and B as transitions to the neutral $\text{Cl}(^2P_{3/2})\cdot\text{H}_2$ and $\text{Cl}^*(^2P_{1/2})\cdot\text{H}_2$ complexes, respectively, with the same assignments holding for the two peaks in the ClD_2^- PE spectrum. In more detail, the $\text{Cl}(^2P_{J=3/2})$ will be split by its interaction with the H_2 into $P=1/2$ (ground) and $3/2$ (excited) states, where P is the projection of J onto the axis between Cl and the H_2 center-of-mass, while the interaction between Cl^* and H_2 results in a single $P=1/2$ state. Since the separation of peaks A and B is so close to the Cl atomic spin-orbit splitting, perturbation of the Cl spin-orbit structure at the geometries probed in this experiment appears to be quite minor. As a result, peaks A and A' should be composed of transitions to the ground $P=1/2$ and $P=3/2$ states, whereas peaks B and B' arise solely from transitions to the upper $P=1/2$ state.

The peaks in the PE spectra can arise from transitions to the neutral van der Waals wells on the ground and spin-orbit excited neutral $\text{Cl}+\text{H}_2$ surfaces, and from transitions to $\text{Cl}+\text{H}_2$ continuum states. This partitioning between bound and continuum states is determined by the projection of the anion vibrational wavefunction onto the various neutral potential energy surfaces. From Bieske's analysis of the infrared spectrum of ClH_2^- ,¹⁰ the anion is linear with a vibrationally-averaged distance between Cl^- and the H_2 center-of-mass of $R_0 = 3.195$ Å for the ground vibrational state, and the radial component of the anion ground state wavefunction for ClH_2^- extends from $R = 2.9$ – 3.5 Å.

Figure 1(b) shows the van der Waals well of the ground state ($P=1/2$) $\text{Cl}+\text{H}_2$ potential energy surface calculated by Bian and Werner (the BW2 surface).¹¹ The minimum of the

van der Waals well corresponds to a T-shaped, C_{2v} structure with $R_e = 3.058 \text{ \AA}$. This value lies well within the range of the anion radial wavefunction. There is a substantial displacement of θ , the angle between the H_2 axis and the axis joining the Cl to the H_2 center-of-mass, from 0° in the anion equilibrium geometry to 90° at the van der Waals minimum. However, recent calculations by Alexander¹⁴ show that the ground state anion wave functions $\psi_0^{(-)}(R, \theta)$ for ClH_2^- and ClD_2^- are quite delocalized, with substantial amplitude covering nearly the entire available range of θ ; the shaded regions in Fig. 1(b) show a contour of $\psi_0^{(-)}(R, \theta)$ for ClH_2^- (*ortho*) for which the amplitude is 15% of the maximum. One therefore expects considerable overlap with the large-amplitude vibrational wave functions supported by the vdW well. The resolution of the PE spectrometer, however, is insufficient to resolve transitions to the individual vdW vibrational states.

Calculations by Aquilanti and co-workers¹⁵ indicate that the excited $P = 3/2$ and $P = 1/2$ $\text{Cl} + \text{H}_2$ surfaces have collinear minimum energy geometries with shallow vdW wells ($\sim 5 \text{ meV}$) and $R_e \approx 3.6 \text{ \AA}$, with the $P = 3/2$ state having a slightly deeper minimum at the collinear geometry than the ground $P = 1/2$ state. As a result, there may be some overlap with the bound vdW states supported by the two excited state potentials, but vertical detachment from the anion (at $R_0 = 3.195 \text{ \AA}$) accesses the repulsive wall in both cases. This will lead to substantial overlap with continuum wavefunctions in the photodetachment transitions to the two excited states.

We are now in a position to consider the features and trends in the PE spectra in more detail, beginning with the energetics. The maxima of peaks A and A' are shifted toward higher eBE from the maxima of atomic Cl^- peaks by 70 meV (565 cm^{-1}) and 85 meV (685 cm^{-1}), respectively, while the onsets of the two peaks are shifted by 460 cm^{-1} from the onsets of the atomic peaks. If there were no interaction between the neutral Cl and H_2 in the FC region, these "solvent shifts" would directly reflect the dissociation energy D_0 of ClH_2^- and ClD_2^- , but, as discussed above, there are weak attractive and repulsive interactions on the neutral surfaces that complicate this picture somewhat. Nonetheless, the solvent shifts of the peak onsets and maxima bracket the dissociation energies D_0 of 499, 559, and 488 cm^{-1} for ClD_2^- (*ortho*), ClD_2^- (*para*), and ClH_2^- (*ortho*), respectively, estimated by Bieske from the effective radial potentials constructed with the help of the anion IR spectrum, as well as the slightly larger values, 527, 604, and 544 cm^{-1} , respectively, obtained in the recent calculation by Alexander.¹⁴ The difference of 60 cm^{-1} between the dissociation energies of ClD_2^- (*ortho*) and ClD_2^- (*para*) is very close to energy interval between the $\text{Cl}^- + \text{D}_2(j=0)$ and $\text{Cl}^- + \text{D}_2(j=1)$ dissociation asymptotes for the *ortho* and *para* species.

One striking feature of the PE spectra is the noticeably broader peaks in the ClD_2^- spectrum compared to ClH_2^- . This may result in part from differing H_2/D_2 nuclear spin populations in ClH_2^- versus ClD_2^- . Bieske observed infrared transitions originating from both ClD_2^- (*ortho*) and ClD_2^- (*para*), while only transitions from ClH_2^- (*ortho*) were seen. The absence of ClH_2^- (*para*) was attributed to its considerably lower D_0 com-

pared to ClH_2^- (*ortho*), (110 cm^{-1} , according to Alexander's calculation¹⁴) combined with the 3:1 *ortho:para* ratio in normal H_2 .

The effect of anion nuclear spin populations on the photoelectron spectrum was discussed previously in the context of FH_2^- ,^{8,16} and similar concepts can be applied to ClH_2^- . We expect the bend wave functions for neutral $\text{Cl} \cdot \text{H}_2$ in the Franck–Condon region to be close to the H_2 free-rotor limit regardless of the neutral electronic state. The narrow peaks in the ClH_2^- PE spectrum suggest that photodetachment is dominated by a transition to a single H_2 rotor state; the $\text{H}_2(j=1)$ and ($j=3$) levels, which would be the lowest rotor states accessible from ClH_2^- (*ortho*), are separated by 0.050 eV (400 cm^{-1}), more than twice the width of peak A or A'. If photodetachment from ClD_2^- (*ortho*) and ClD_2^- (*para*) were dominated by transitions to the $\text{D}_2(j=0)$ and 1 rotor levels, respectively, these transitions would be separated by 60 cm^{-1} (7.4 meV), and would presumably not be resolved in our PE spectrometer. The net result is a broadening of all ClD_2^- transitions due to the presence of two nuclear spin species, as opposed to only one in ClH_2^- .

The broadening may also have its origins in the excited state transitions. Bieske¹⁰ has shown that the effective radial potential for ClD_2^- is deeper than that for ClH_2^- , and the radial wave function is shifted toward slightly smaller values of R . This results, for example, in a lower value of R_0 for ClD_2^- , 3.159 \AA versus 3.195 \AA for ClH_2^- . Photodetachment of ClD_2^- therefore samples more of the repulsive wall and less of the vdW well for the neutral $P = 3/2$ and $1/2$ excited states, broadening peaks B' and A' with respect to peaks B and A. The relative importance of these two possible origins of the differential broadening can be determined in quantum mechanical simulations of the PE spectra, and these are currently being carried out by Alexander and Manolopoulos.¹⁷ In addition, planned experiments in which ClH_2^- (*para*) is generated using *para*- H_2 as the expansion gas will directly address the effect of nuclear spin statistics on the PE spectra.

Finally, we consider the results obtained here with our previous PE spectra of FH_2^- .^{8,16} There are two significant differences between the spectra. In the FH_2^- spectra, perturbation of the F atomic spin–orbit fine structure by the H_2 is significant; the spin–orbit excited states were found to be strongly repulsive in the Franck–Condon region and well-separated from the ground state transitions, even though the spin–orbit splitting in F is only about half that of Cl. This difference occurs because the FC region for FH_2^- photodetachment overlaps the $\text{F} + \text{H}_2$ transition state, near which the spin–orbit excited states diverge significantly from the ground state.¹⁵

The other important difference is that the FH_2^- ground state spectrum is composed of partially resolved progressions in what are essentially H_2 nearly free-rotor levels, the envelope of which covers almost 0.2 eV , i.e., an order of magnitude broader than peak A in the ClH_2^- spectrum, regardless of whether *para*- or *normal*- H_2 was used. These progressions resulted from a change of geometry between the linear FH_2^-

anion and bent FH_2 transition state, for which the F–H–H angle is 119° . In contrast, peak A in the ClH_2^- shows no evidence for an analogous hindered rotor progression, even though there is a larger change in angle between the anion and vdW minimum. This somewhat surprising result may reflect the more delocalized bend wavefunction in ClH_2^- compared to FH_2^- , resulting in part from the considerably higher dissociation energy of 0.20 eV for FH_2^- .⁶ A more quantitative assessment of this effect will require full quantum mechanical simulation of the ClH_2^- PE spectrum; these calculations are currently in progress.¹⁷

In summary, the ClH_2^- and ClD_2^- PE spectra presented here represent the first experimental probe of the $\text{Cl}+\text{H}_2$ prereactive van der Waals region and of the low-lying $\text{Cl}+\text{H}_2$ spin-orbit excited states, thus providing new information on two key aspects of the $\text{Cl}+\text{H}_2$ reaction dynamics. The work described here represents the first step in the spectroscopic characterization of the potential energy surfaces of this benchmark reaction. Planned future experimental directions include (a) measuring the photoelectron spectrum of $\text{Cl}^- \text{H}_2(\textit{para})$, by using *para*- H_2 as the expansion gas, and (b) performing zero electron kinetic energy spectroscopy experiments on ClH_2^- which should resolve any low-frequency van der Waals progressions that are contributing to the peaks in the photoelectron spectra.

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