The covalent interaction between dihydrogen and gold: A rotational spectroscopic study of H₂–AuCl

Daniel A. Obenchain,^{1,a)} Derek S. Frank,^{1,b)} G. S. Grubbs II,² Herbert M. Pickett,¹ and Stewart E. Novick¹

¹Department of Chemistry, Hall-Atwater Laboratories, Wesleyan University, 52 Lawn Ave., Middletown, Connecticut 06459, USA

²Department of Chemistry, Missouri University of Science and Technology, 400 W. 11th Street, Rolla, Missouri 65409, USA

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The pure rotational transitions of H₂–AuCl have been measured using a pulsed-jet cavity Fourier transform microwave spectrometer equipped with a laser ablation source. The structure was found to be T-shaped, with the H–H bond interacting with the gold atom. Both ³⁵Cl and ³⁷Cl isotopologues have been measured for both *ortho* and *para* states of H₂. Rotational constants, quartic centrifugal distortion constants, and nuclear quadrupole coupling constants for gold and chlorine have been determined. The use of the nuclear spin-nuclear spin interaction terms D_{aa} , D_{bb} , and D_{cc} for H₂ were required to fit the *ortho* state of hydrogen, as well as a nuclear-spin rotation constant C_{aa} . The values of the nuclear quadrupole coupling constant of gold are $\chi_{aa} = -817.9929(35)$ MHz, $\chi_{bb} = 504.0(27)$ MHz, and $\chi_{cc} = 314.0(27)$. This is large compared to the eQq of AuCl, 9.63 312(13) MHz, which indicates a strong, covalent interaction between gold and dihydrogen. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4983042>]

I. INTRODUCTION

From 2000 to 2004, Gerry and co-workers reported a series of Ng–MX complexes in the gas phase using Fourier transform microwave (FTMW) spectroscopy, where M is a coinage metal from group 11 and X is a halide.^{1–7} In these complexes, Ng = Ar, Kr, or Xe and the Ng-metal dissociation energy, D_e , was predicted between 20 and 100 kJ mol^{−1}. Through spectroscopic measurements and quantum chemical calculation, the Ng–M interaction in these complexes was found to be weakly covalent. The only comparable studies to the Ng–MX systems done by Gerry are Ar–Hg⁸ and Ar–NaCl.⁹ Unlike the coinage metal studies, these systems were found to have van der Waals interaction energies (≤ 18 kJ mol^{−1})¹⁰ and larger Ar–M distances. More recently, Walker, Legon, and co-workers have investigated the MX interaction with both polar^{11–20} and non-polar polyatomic molecules.^{21–23}

In all MX studies listed above, the nuclear quadrupole coupling constant (NQCC), or eQq , has served as a probe for the change in the electronic structure of the metal when present. This occurs for those systems where M = Cu or Au (⁶³Cu/⁶⁵Cu and ¹⁹⁷Au have nuclear spins of $I = 3/2$). The measurable NQCC components serve as a direct probe of the electric field gradient at the nucleus of the metal. A study of multiple AuX and CuX complexes explores how interactions, from van der

Waals to covalent bonding, can change the field gradient in a given system.

In the case of molecular hydrogen complexes, previous studies using high resolution spectroscopy are few in number. The weak van der Waals complexes of H₂–OCS,^{24–26} H₂–HCN,²⁷ H₂–H₂O,²⁸ and H₂–HCCCN²⁹ all reported vastly different rotational constants for their respective measurements of the *ortho* and *para* species of H₂. In the case of H₂–HCN, the authors report that H₂ must be bound to different ends of HCN, H in *para*-H₂, N in *ortho*-H₂. The differences in the spectroscopic constants of the *ortho* and *para* species of the complexes above are large compared to those of H₂–AgCl,³⁰ where the *ortho/para* difference is small, and the *ortho/para* states can be fit as one species with the same rotational constants for both states of hydrogen. This difference in how *ortho/para* fits are handled suggests that H₂ must be more tightly bound in the latter complex and have the same geometry for each state.

Continuing a series of studies on the complexes formed between H₂ and metal halides, we report here the rotational spectrum of H₂–AuCl. Both the *ortho* and *para* states have been measured for the first time using Fourier transform microwave spectroscopy, and the changes in the nuclear quadrupole interaction of gold are used to explore the strong, covalent interaction of dihydrogen to the metal halide.

II. EXPERIMENTAL

All rotational transitions were measured on a Balle-Flygare type cavity spectrometer³¹ at Wesleyan University, which operates in the 6–26.5 GHz frequency range. The instrument is housed in a high-vacuum chamber (better than 10^{−6}

^{a)}Present address: Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz-Universität, Callinstrasse 3A, D-30167 Hannover, Germany.

^{b)}Present address: Department of Chemistry and the Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109, USA.

Torr) and is a Fabry-Perot microwave cavity formed by two 35.6 cm diameter aluminum mirrors each with a spherical radius of curvature of 84.0 cm. The subtleties of the design are given in the work of Hight Walker *et al.*³² and the instrument modeled after the design of the National Institute of Standards and Technology pulsed-jet FTMW spectrometer.³³ The spectrometer is equipped with a laser ablation source,³⁴ utilizing the fundamental of a Nd:YAG laser at 1064 nm. A gold-tipped aluminum rod was used as the source of gold for the laser ablation technique. Mixtures of H₂ (Airgas®, >99%) and Cl₂ (Sigma-Aldrich®, 99.5%) were diluted in Ar (Airgas, 99.999%). Concentrations of H₂ and Cl₂ were controlled using a gas flow controller.³⁰ High purity Ar was preferred to minimize the moisture present, which made Cl₂ less corrosive to the system. Optimal line intensities were achieved with 7%-9% H₂ and <0.1% Cl₂ in Ar held at a backing pressure of 5.5 atm, and the molecular beam is pulsed along the axis of the resonant cavity, producing molecular signals that are observed as Doppler doublets. The absolute concentration of Cl₂ was unknown, as Cl₂ was flowed at the controller's lower limit, 1 standard cm³/min, preventing accurate knowledge of the concentration.

III. QUANTUM CHEMICAL CALCULATIONS

All quantum chemical calculations were performed using the GAUSSIAN 09 Revision D suite.³⁵ Structure optimizations and zero-point energy (ZPE) corrections were completed on the H₂, AuCl, H₂-AuCl structures at the MP2 level of theory. For H and Cl atoms, an aug-cc-pVQZ basis set was used. For Au atoms, an electric core potential, ECP60MD-AVQZ,³⁶ was used with an aug-cc-VQZ-pp^{36,37} basis set obtained from the EMSL Basis Set Exchange.^{38,39} Anharmonic frequencies were also calculated at this level of theory, providing an estimate of the quartic centrifugal distortion constants.

Optimizations produced a T-shaped structure, with the top of the T being the H₂ ligand as shown in Figure 1. This structure is consistent with those observed in previous metal halide hydrogen complexes.^{30,34} The binding energy D_e was calculated to be 164 kJ/mol. There is also a predicted elongation of the H₂ bond upon formation of the complex from 0.795 Å in free H₂⁴⁰ to an r_e value of 0.91 Å. The spectroscopic constants of H₂-AuCl predicted in this calculation are presented alongside the experimentally determined values in Table I.

FIG. 1. Structure obtained from MP2 level optimization. Predicted Au-Cl bond length is 2.19 Å and predicted H-H bond length is 0.91 Å. The distance from the Au nucleus to the H-H bond is predicted to be 1.55 Å.

TABLE I. Spectroscopic parameters for H₂-AuCl.

	Predicted ^a	H ₂ -Au ³⁵ Cl	H ₂ -Au ³⁷ Cl
A (MHz)	1 209 646	1 209 646	1 209 646 ^b
B (MHz)	3 374.399	3 297.117(21) ^c	3 150.87(13)
C (MHz)	3 365.012	3 287.332(21)	3 141.62(13)
D_J (MHz)	0.000 92	0.000 935(23)	0.000 869(33)
D_{JK} (MHz)	0.240	0.168 53(22)	0.161 83(49)
χ_{aa} (Cl) (MHz)	-37.09	-41.687 7(35)	-32.871 7(52)
χ_{bb} (Cl) (MHz)	16.02	18.581(11)	14.73(16)
χ_{cc} (Cl) (MHz)	21.07	23.107(11)	18.14(16)
χ_{aa} (Au) (MHz)	-6.31	-817.992 9(35)	-818.012 3(52)
χ_{bb} (Au) (MHz)	7.40	504.0(27)	490(17)
χ_{cc} (Au) (MHz)	-1.09	314.0(27)	328(17)
$\chi_{aa} D_k$ (Au) (MHz)	N/A ^d	-1.874 9(90)	-1.874 9 ^e
D_{aa} (H ₂) (MHz)	N/A	0.174 6(84)	0.148(15)
D_{bb} (H ₂) (MHz)	N/A	-0.313(14)	-0.33(22)
D_{cc} (H ₂) (MHz)	N/A	0.138(16)	0.18(23)
C_{aa} (H ₂) (MHz)	N/A	-0.086 4(29)	-0.086 4 ^e
N^f	...	59	27
RMS ^g (kHz)	...	2.9	2.3

^aFrom MP2 level calculation.

^bHeld to the value obtained from MP2 level calculation.

^cNumbers in parentheses give standard errors (1σ , 67% confidence level) in units of the least significant figure.

^dN/A values cannot be directly obtained from calculation.

^eHeld to the value obtained from the H₂-Au³⁵Cl fit.

^fNumber of transitions assigned.

^gRoot mean square deviation of the fit, $\sqrt{(\sum [(obs-calc)^2] / Nlines)}$.

IV. THE NUCLEAR QUADRUPOLE COUPLING CONSTANT OF GOLD

From previous Ng-AuCl studies^{2,41,42} and the H₂-CuF³⁴ work, the value of the gold NQCC in H₂-AuCl was expected to be large compared to that of free AuCl. χ_{aa} of ⁶³Cu in H₂-CuF was a factor of 3 larger than that of free CuF. The *ab initio* χ_{aa} value of the Au atom in H₂-AuCl gave an unexpectedly low value. Reported values of eQq for rare gas ligands binding with the gold of AuCl were on the order of hundreds of MHz, while the monomer eQq value was reported as 9.63 312(13) MHz.⁴¹ The predicted χ_{aa} of H₂-AuCl from theory is -6.31 MHz. There is a trend apparent in Table II, where increasing experimental values of D_e in the complex trend with decreasing values (more negative) of ¹⁹⁷Au eQq_{aa} , where D_e is defined as the energy needed to separate the metal halide from the noble gas or hydrogen molecule to infinite distance. This leaves the prediction of χ_{aa} of Au in H₂-AuCl as an obvious outlier, with a predicted interaction energy of 164 kJ/mol (D_e). Another trend is observed with the value of ¹⁹⁷Au eQq increasing as the value of ³⁵Cl eQq decreases in AuCl complexes. Both trends are plotted in Figures 2 and 3. Regression analyses were used to fit both sets of data to a straight line, from which a prediction of χ_{aa} of gold could be interpolated. These predictions yield values of χ_{aa} (Au) of -909 MHz from interpolation with D_e data and -792 MHz from interpolation with eQq ³⁵Cl data. Both are significantly closer to the value determined from spectroscopic analysis, -817.9929(35) MHz, than the value of -6.31 MHz predicted from quantum chemical calculations. The chosen electric core potential for gold in the *ab initio* calculation seems to give accurate

TABLE II. Comparison of ^{197}Au and ^{35}Cl eQq values and D_e values from previous studies compared to the predicted values for $\text{H}_2\text{-AuCl}$.

	eQq_{aa} ^{197}Au (MHz)	eQq_{aa} ^{35}Cl (MHz)	D_e (kJ/mol) ^a	Reference
AuCl	9.633 12(13) ^b	-61.996 94(81)	0 ^c	Evans and Gerry ⁴¹
Ar-AuCl	-259.835 2(21)	-54.050 2(31)	46.9	Evans <i>et al.</i> ²
Kr-AuCl	-349.857(23)	-52.012(21)	71.3	Evans <i>et al.</i> ²
CO-AuCl	-1 025.975 3(29)	-36.388 4(34)	182 ^d	Evans <i>et al.</i> ⁴² and Antes <i>et al.</i> ⁴³
$\text{H}_2\text{-AuCl}$ (<i>ab initio</i>) ^e	-6.31	-40.6	164	
$\text{H}_2\text{-AuCl}$ (interpolated) ^g	-909	...	...	
$\text{H}_2\text{-AuCl}$ (interpolated) ^h	-792	...	...	
$\text{H}_2\text{-AuCl}$ (experimental) ⁱ	-817.992 9(35)	-41.687 7(35)	...	

^aThe value of D_e is the energy required to separate each species such that the AuCl monomer and the complex binding partner are at infinite distance.

^bNumbers in parentheses give standard errors (1σ , 67% confidence level) in units of the least significant figure.

^cThe values of D_e for the monomer are assumed to be zero for the interpolation.

^dFrom CCSD(T) result of the optimized MP2 structure.

^eValues obtained from *ab initio* calculations.

^fFor the T-shaped $\text{H}_2\text{-AuCl}$, the value of χ_{aa} is reported.

^gValues extrapolated from a plot of D_e vs $\chi_{aa}^{197}\text{Au}$ using the *ab initio* value of D_e to obtain a predicted $\chi_{aa}^{197}\text{Au}$ value.

^hValues extrapolated from a plot of the experimental $\chi_{aa}^{35}\text{Cl}$ vs $\chi_{aa}^{197}\text{Au}$ using the *ab initio* value of $\chi_{aa}^{35}\text{Cl}$ to obtain a predicted $\chi_{aa}^{197}\text{Au}$ value.

ⁱThis work.

structures for the molecular systems and energy but does poorly at predicting the gold NQCCs. Currently, techniques are in development that show promise for predicting the quadrupole coupling constants of metals like gold and copper but are not currently available.⁴⁴ There has been some success reported in using *ab initio* methods to predict fairly accurate NQCCs of OC-AuCl ⁴⁵ and of AuF complexes,⁴⁶ but these methods were more computationally complex than those were needed in this study.

FIG. 2. (a) eQq_{aa} of ^{197}Au is compared to the D_e of various AuCl complexes. For the monomer AuCl, D_e is set to zero. A linear equation of the line that best fits the data points is $eQq(^{197}\text{Au}) = -5.54(13) \frac{\text{MHz}}{\text{kJ/mol}} \cdot D_e$ with an $R^2 = 0.998$. The intercept of this line is forced to be zero. The green square is the value predicted by *ab initio*. The red circle is the experimentally measured value.

As a check of the quality of the prediction, regression analysis was performed again, this time with the inclusion of the experimental data from this work. The equation of the line that could be used to predict eQq ^{197}Au from *ab initio* D_e values went from $eQq(^{197}\text{Au}) = -5.54(13) \frac{\text{MHz}}{\text{kJ/mol}} \cdot D_e$ without experimental $\text{H}_2\text{-AuCl}$ data to $eQq(^{197}\text{Au}) = -5.65(16) \frac{\text{MHz}}{\text{kJ/mol}} \cdot D_e$ with $\text{H}_2\text{-AuCl}$ data. The value of R^2 differed only slightly, decreasing from $R^2 = 0.998$ to $R^2 = 0.996$, respectively. The change in the equation of the line and R^2 value is similar in the prediction based on the value of ^{35}Cl eQq , where

FIG. 3. eQq_{aa} of ^{197}Au is compared to eQq_{aa} of ^{35}Cl for reported AuCl species. The linear equation that best fits the previously reported values is $eQq(^{197}\text{Au}) = -41.0(18) \cdot eQq(^{35}\text{Cl}) - 2501(96)$ MHz with an $R^2 = 0.996$. The green square is the value predicted by *ab initio*. The red circle is the experimentally measured value.

$eQq^{197}(\text{Au}) = -41.0(18) \cdot eQq(^{35}\text{Cl}) - 2501(96)$ MHz with an $R^2 = 0.996$ fits the data without the experimental $\text{H}_2\text{-AuCl}$ data and with this data becomes $eQq^{197}(\text{Au}) = -41.4(15) \cdot eQq(^{35}\text{Cl}) - 2529(75)$ MHz with an $R^2 = 0.996$.

V. RESULTS

Initial scans for $\text{H}_2\text{-AuCl}$ in the 13 GHz region of the spectrum revealed groups of hyperfine split transitions. There were different magnitudes of the splitting suggesting that there were multiple hyperfine interactions. The largest set of splittings was on the order of hundreds of MHz. Based on the results of previous AuCl studies, we assumed that this splitting was from the NQCC of the gold atom. The next largest splitting was on the order of tens of MHz, which is consistent with that of a chlorine nucleus in a σ -bond environment.⁴⁷ Further measurements revealed not only Doppler splitting, which is expected in a coaxially aligned cavity instrument, but an additional <1 MHz splitting for only some of the transitions. This follows the observation from the work on $\text{H}_2\text{-AgCl}$ where *ortho*- $\text{H}_2\text{-AgCl}$ transitions had an additional splitting due to the nuclear spin-nuclear spin interaction and *para*- $\text{H}_2\text{-AgCl}$ did not.

To obtain a correct assignment of observed transitions, the additional splitting described above was used to decide which transitions should be labeled as *ortho* and *para*. This was a crucial step in the fitting process, as it was expected that hyperfine split transitions with these nuclear spin-nuclear spin interactions would have $K_a = 0$ (*para*- $\text{H}_2\text{-AuCl}$) and $K_a = 1$ (*ortho*- $\text{H}_2\text{-AuCl}$) transitions overlapping. For the transitions of $J = 1-0$, there are only transitions involving $K_a = 0$ states, which therefore must be from *para*- $\text{H}_2\text{-AgCl}$. These transitions served as a check of initial assignments allowing for accurate assignment of $K_a = 0$ for all observed J transitions. Any remaining transitions not assigned to the *para* state were assumed to be from the *ortho* state. The spectral fitting for both the ^{35}Cl and ^{37}Cl isotopologues was carried out using Pickett's SPFIT/SPCAT software package^{49,50} using a Watson S-reduced Hamiltonian in the I' representation. A total of 86 hyperfine split transitions from the $J = 3-2$, $2-1$, and $1-0$ were observed for both isotopologues. The measured transitions observed dependence on the A rotational constant, and this value was held at the value of the *ab initio* prediction, 1 209 646 MHz. The B and C rotational constants were fit, along with the quartic centrifugal distortion constants D_J and D_{JK} . The fits of *ortho* and *para* species were combined into a single fit, which was dependent on the D_{JK} term. Only transitions from the $K_a = 0$, 1 levels were observed. Searches were carried out for the $K_a = 2$ transitions of the $J = 3-2$ levels, but none were observed despite considerable averaging. The coupling scheme used in the fits was $\mathbf{J} + \mathbf{I}_{(\text{Cl})} = \mathbf{F}_1$, $\mathbf{F}_1 + \mathbf{I}_{(\text{Au})} = \mathbf{F}_2$, and $\mathbf{F}_2 + \mathbf{I}_{(\text{H}_2)} = \mathbf{F}_{\text{TOT}}$. A complete set of line lists are available in Tables I and II of the [supplementary material](#).

NQCCs for both chlorine, χ_{Cl} , and gold, χ_{Au} , nuclei were fit. The inclusion of a first order correction in K^2 was added for the NQCC of gold, with a reported value of $-1.8749(90)$ MHz. There was no dependence of the off-diagonal NQCC components in either gold or chlorine. The magnetic nuclear spin-nuclear spin interaction tensor ($\mathbf{D}$) was fit for the

hydrogen-hydrogen interaction (both $I = 1/2$). The terms D_{aa} , D_{bb} , and D_{cc} depend only on transitions of *o*- $\text{H}_2\text{-AgCl}$. It was also found that these transition frequencies had a small dependence on the nuclear spin rotation term, C_{aa} , for hydrogen, which is identical for each hydrogen nucleus by the C_{2v} symmetry of the molecule. Results of the spectral fits are compared alongside the *ab initio* results in Table I. The spin-rotation term was only necessary for transitions of *o*- $\text{H}_2\text{-AgCl}$. Fitting of terms to only specific spin states, as was done in the $\text{H}_2\text{-AgCl}$ paper,³⁰ requires special considerations in Pickett input files. This procedure is described in the Cologne Database,⁵¹⁻⁵³ but for clarity the fit files for $\text{H}_2\text{-Au}^{35}\text{Cl}$ used in this work are included in the [supplementary material](#).

VI. STRUCTURE

The T-shaped structure predicted in the *ab initio* calculation is confirmed by the spectroscopic results. The lack of off-diagonal NQCC terms is consistent with this symmetry. As the A rotational constant is significantly large, the more massive Au and Cl nuclei must lie along the a -axis. As the hydrogen nuclei are observed to be *ortho* for $K_a = 1$ and *para* for the $K_a = 0$ transitions, they must exchange upon rotation about this axis and must be symmetric about the a -axis. Thus the hydrogens must form the top of the T in this T-shaped structure.

Information on $r_{\text{H-H}}$ is contained in the nuclear spin-nuclear spin interaction terms of $\text{H}_2\text{-AuCl}$. As was reported in the study of $\text{H}_2\text{-AgCl}$,³⁰ the nuclear spin-nuclear spin interaction terms along the H-H bond are related by,

$$D_{ii} \propto \frac{1}{r_{\text{H}_2}^3}, \quad (1)$$

where D_{ii} is the i th component of the spin-spin tensor. In the case of the $\text{H}_2\text{-AuCl}$ complex, this is the D_{bb} component (see Figure 1). If this is compared directly to a measured spin-spin term for free H_2 (which is D_{aa}), the change in $1/r_{\text{H}_2}^3$ can be determined by

$$r_0(\text{H}_2 \text{ in complex}) = r_0(\text{Free H}_2) \times \left(\frac{D_{aa}(\text{Free H}_2)}{D_{bb}(\text{H}_2 \text{ in complex})} \right)^{1/3}. \quad (2)$$

The calculated r_0 values for $\text{H}_2\text{-AuCl}$ are presented in Table III, alongside the results of the most abundant isotopologue of $\text{H}_2\text{-AgCl}$. For H-H bond lengths, r_0 values between 0.8 Å and 1.0 Å are considered to be slightly elongated “Kubas-type” bonds, while r_0 values between 1.0 Å and 1.25 Å are considered to be “stretched dihydrogen”, and r_0 values between 1.25 Å and 1.6 Å are termed as compressed hydrides.⁵⁷ This places the measured values of the two isotopologues, 0.92(1) Å and 0.95(4) Å, respectively, on the upper end of the Kubas region. There was not enough isotopic data available to complete least-squares structural fitting procedures with this system with decent certainty. Only the ^{197}Au isotope is observable in natural abundance in gold containing species, and due to the corrosive nature of Cl_2 in the instrument's sampling system, searches of the HD and D_2 complexes were not completed in this study.

TABLE III. H–H distances determined from nuclear spin-nuclear spin interaction (D_{aa} and D_{bb}) terms.

	D_{aa} (or D_{bb}) (kHz)	r_0 (H_2) (Å)	Percent increase	Reference
			from free H_2^a (%)	
Free H_2 (theory)	−576.8	0.75095	...	Ramsey ⁴⁰
Free H_2 (expt.)	−576.8(4) ^b	0.7468(5)	0	Harrick <i>et al.</i> ⁴⁸
H_2 – ¹⁰⁷ Ag ³⁵ Cl	−459(4)	0.812(2)	8.73(2)	Grubbs II <i>et al.</i> ³⁰
H_2 –Au ³⁵ Cl	−313(14)	0.92(1)	23.2(2)	This work
H_2 –Au ³⁷ Cl	−326(18)	0.95(4)	27(1)	This work

$$^a \left[\frac{r_0(\text{complex } H_2)}{r_0(\text{free } H_2)} - 1 \right] \times 100\%.$$

^bNumbers in parentheses give standard errors (1σ , 67% confidence level) in units of the least significant figure.

VII. COVALENT BONDING STRENGTH OF DIHYDROGEN TO GOLD CHLORIDE

The pseudo-diatomic model uses experimental structures and spectroscopic constants to determine the intermolecular binding energy in weakly bound complexes, that is, the energy required to separate the two monomer units in the complex to infinite distance.^{60,61} This model was intended for weakly bound complexes free of covalent interactions between molecules where the a -axis lies nearly co-linear between the centers of mass of the two molecules. In a van der Waals system, the distortion term that accounts for the stretching complex as it rotates (D_J) is dominated by the stretching along the intermolecular “bond” formed between

the two species, assuming that the individual species distort significantly less at higher rotational states. In the dihydrogen metal halide complexes, and perhaps most of the noble metal halide complexes, the intermolecular bond is strong enough that D_J has significant contribution from the stretching of the individual molecules, making the assumption that D_J is dominated by intermolecular interactions incorrect for strongly bound systems of more than two molecules.

An alternative method for the determination of binding energy is to use *ab initio* methods. There are over a dozen studies of metal halide (MX) interactions with noble gases and noble gases or simple molecules, all with a general trend of relatively strong interaction/binding energies between the MX species and its partner species. Table IV shows *ab initio* predictions of D_e for many different compounds. A general trend can be seen for noble gas complexes of metal halides with polarizability. For example, in CuF–Nb species with Ar, Kr, and Xe, the binding energy increases from 44 kJ/mol to 48 kJ/mol and 59 kJ/mol. In this case, the trend of increasing binding energy follows the trend of increasing polarizability of the progressively larger noble gas atoms. If this trend were to transfer to H_2 species, it would be expected that the H_2 bond interaction energy be low, as the perpendicular polarizability of H_2 is $0.69 \times 10^{-24} \text{ cm}^3$, compared to that of argon, $1.63 \times 10^{-24} \text{ cm}^3$.⁶² However, *ab initio* results suggest that the binding energy of the H_2 complexes is much larger than polarizability trends would predict. This is seen in Table IV, where

TABLE IV. The dissociation energies of different MX complexes and their energies normalized by the appropriate polarizability of the non-metal containing molecule that forms the complex.

Metal halide	Complex	Complex dissociation energy (kJ/mol)	Dissociation energy scaled by polarizability (kJ/mol Å ³)	Reference
CuF	Ar	44	27	Thomas <i>et al.</i> ⁶
CuCl	Ar	33	20	Thomas <i>et al.</i> ⁶
AgF	Ar	14	9	Thomas <i>et al.</i> ⁶
AgCl	Ar	16	10	Lovallo and Klobukowski ⁵⁸
AuF	Ar	55	34	Thomas <i>et al.</i> ⁶
AuCl	Ar	42	26	Thomas <i>et al.</i> ⁶
CuF	Kr	48	19	Lovallo and Klobukowski ⁵⁸
CuCl	Kr	39	16	Lovallo and Klobukowski ⁵⁸
AgF	Kr	17	7	Thomas <i>et al.</i> ⁶
AgCl	Kr	15	6	Thomas <i>et al.</i> ⁶
AgBr	Kr	17	7	Lovallo and Klobukowski ⁵⁸
AuF	Kr	58	23	Thomas <i>et al.</i> ⁶
AuCl	Kr	44	18	Thomas <i>et al.</i> ⁶
CuF	Xe	59	15	Lovallo and Klobukowski ⁵⁸
CuCl	Xe	51	13	Thomas <i>et al.</i> ⁶
AgF	Xe	43	11	Lovallo and Klobukowski ⁵⁸
AgCl	Xe	39	10	Lovallo and Klobukowski ⁵⁸
AuF	Xe	101	25	Cooke and Gerry ⁷
AuCl	Xe	80	20	Lovallo and Klobukowski ⁵⁸
CuF	N ₂	139	63	Francis <i>et al.</i> ²²
CuF	CO	150	65	Bera <i>et al.</i> ⁵⁹
CuF	H ₂	60.2	91	Frohman <i>et al.</i> ³⁴
AgCl	H ₂	71	108	Grubbs <i>et al.</i> ³⁰
AuCl	H ₂	164	249	This work

the predicted binding energy of each metal halide is scaled by its respective polarizability.

Further indication that the binding strength of H₂ to AuCl is at least weakly covalent is the change in the NQCC of gold. Using the line plotted in Figure 2 proved an accurate way to predict the NQCC of gold. Once this value is determined experimentally, it can be used to back out a value of D_e , which is found to be 147(3) kJ/mol and an error in the *ab initio* value of 11%. This would be a more reliable estimation of D_e if the plot of D_e against eQq_{aa} ¹⁹⁷Au did not already contain *ab initio* data points. Considering either the direct prediction of D_e = 164 kJ/mol or the interpolated value of 147(3) kJ/mol, the binding energy is in the range of a weak covalent interaction.

VIII. CONCLUSION

The assignment of the rotational transitions of H₂–AuCl has yielded structural and electronic changes in H₂ and AuCl. Assignment of the transitions was aided by *ab initio* predictions. These predictions agree well with the experiment except in the case of the NQCC of gold, where an extrapolation of the corresponding chlorine NQCC or binding energy of the complex gave a better prediction of the experimental value by two orders of magnitude. An interpolation of the NQCC from previous studies was used to improve the predicted value of the gold NQCC. Using either the NQCC of chlorine and dissociation energy yielded predictions that were over two orders of magnitude better than the chosen *ab initio* method.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for line lists and the .lin and .par files used for the fitting of H₂–Au³⁵Cl.

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