

Dipole moment analysis of excited van der Waals vibrational states of ArH^{35}Cl

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The far-infrared laser electric resonance spectra of the prototypical atom-diatom complex ArH^{35}Cl are analyzed using improved zero-field molecular constants, yielding accurate permanent and transition dipole moments for the three lowest excited van der Waals vibrational states. The constants are obtained from a multistate fit to previous microwave, far-infrared laser electric resonance, and far-infrared tunable laser spectra, as well as new far-infrared measurements of the Σ -stretch state, which are reported here. The signs of the dipole moments and Coriolis coefficients establish the relative orientations of the HCl subunit in these states. The fit is found to converge only if these signs correspond to the HCl pointing in opposite directions along the a inertial axis in the Σ -stretch and Σ -bend states. A weak preference, near the experimental error limit, is found for the Ar-Cl-H average angle in the Π -bend state to be greater than 90° , contrary to expectation. For the best fit, we obtain the a -axis dipole moment components $-0.5413(11)$ D (Σ bend), $-0.26345(29)$ D (Π bend), and $0.6754(36)$ D (Σ -stretch); and the b -axis components $0.365(12)$ D (Π and Σ -bend) and $-0.0465(43)$ D (Π and Σ stretches), where the signs of the Coriolis coefficients and μ_a for the Σ stretch have been arbitrarily fixed positive. For the expected Π -bend configuration, with the Ar-Cl-H angle less than 90° , the magnitudes along the a axis change only slightly, but the b -axis components become $0.149(12)$ and $-0.1403(64)$ D for the Π - Σ -bend and Π - Σ -stretch interactions, respectively.

I. INTRODUCTION

The potential energy surface for the van der Waals coordinates of ArHCl is perhaps the most thoroughly studied of any atom-diatom complex. This is due in large part to significant efforts by Hutson and Howard^{1,2} and Hutson³⁻⁵ to develop semiempirical potential energy surfaces that could be fit directly to the experimental observables. Early efforts were confined to the assumption of rigid HCl, for which the potential surface is defined only by the coordinates R and θ as defined in Fig. 1, although the most recent work adds the internal HCl stretching coordinate to these degrees of freedom.⁵

The forces binding the subunits of this system are generally divided into isotropic components, independent of θ , and anisotropic components. It is convenient to consider the states of the complex in the limit where the anisotropy is zero, and the internal torsions of ArHCl are identically described by freely rotating HCl. The ground state corresponds to the $j=0$, $m_j=0$ level, and the lowest torsional states to $j=1$, $|m_j|=0$ and 1 , with m_j defined as the projection of the HCl rotational angular momentum j on the a inertial axis of the complex. Anisotropy has the effect of coupling states of different j , but with m_j a constant of the motion, and we label the resulting eigenstates as Σ or Π for $|m_j|=0$ or 1 , respectively.

The ground state is found to be a hydrogen-bonded

system, indicating substantial anisotropy at the zero-point energy, although with large amplitude oscillations about $\theta=0^\circ$. In contrast, the lowest excited torsional states, the Π - and Σ -bend (Σ_b) states corresponding to the $j=1$, $m_j=0$ and $|m_j|=1$ rotational states of free HCl, respectively, are virtually unhindered by the anisotropic terms in the potential energy. The energy levels of these states are drawn in Fig. 2 together with the ground (Σ_0) and first excited stretching (Σ_s) states. The similarity between the free rotor $j=1 \leftarrow 0$ transition energy of 21 cm^{-1} and the Π and Σ_b excitation energies of $23\text{--}34\text{ cm}^{-1}$ qualitatively illustrates the high degree of isotropy of this potential energy surface, compared to those of chemically bonded systems.

Although the geometry of the ground state (Σ_0) was deduced from experiment nearly 20 years ago by Novick *et al.*,^{6,7} with subsequent work by Hutson and Howard,⁸ the excited states of the van der Waals vibrations were first probed directly more than a decade later in pioneering studies of the Π state by Marshall *et al.*⁹ and Ray *et al.*¹⁰ Some of these transitions were later reassigned based on double resonance experiments,¹¹ but the principal results remain unchanged. The lack of tunable far-infrared radiation sources required the vibrational studies to be carried out at high electric fields in order to Stark tune the transitions into resonance with one of the available fixed-

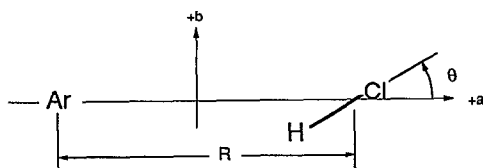


FIG. 1. The coordinate system used to describe the ArHCl van der Waals potential energy surface. R is the separation between the Ar and HCl center of mass, and θ is the angle between the HCl and ArHCl inertial a axes.

frequency laser transitions. The Berkeley group laser electric resonance (LER) experiments were then extended to measurements of the Σ_b (Ref. 12) and Σ_s (Ref. 13) states of the molecule, evaluating directly their vibrational band origins, rotational constants, quadrupole coupling constants, and permanent dipole moments. However, the interpretation of the LER spectra was impaired by the low number of accessible rovibrational components and the complexity of the Stark effect. The Coriolis coupling of the Σ_b and Σ_s states with the Π state could not be separated, and in the effective Hamiltonian for the Stark effect, couplings between these vibrational states were neglected. These couplings arise from the perpendicular transition dipole moments μ_b between the Π and either excited Σ state. Although the same interaction is well-resolved in the lowest bending states in ArHCN,¹⁴ in ArHCl the bending states are separated by 10 cm^{-1} , six times the separation in ArHCN, and the available data are less precise by a factor of 100. This is partly compensated for by the relatively high fields of the LER work (up to 20 kV/cm), and we estimated that μ_b values should be determinable from that data.

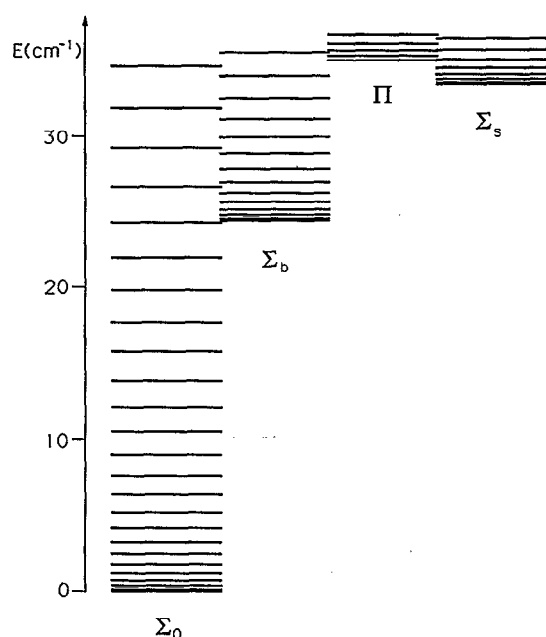


FIG. 2. Energy level diagram, including rotational structure, for ArHCl illustrating the states discussed in this report.

Subsequent to the LER experiments, tunable far-infrared lasers provided straightforward measurements of the transitions from the ground state to the Σ_b ,¹⁵ Π ,¹⁶ and Σ_s states in zero electric field. In addition, there are extremely high-precision pure rotational spectra of the two excited Σ states in the microwave by Chuang and Gutowsky.¹⁷ Reeve *et al.*¹⁶ took advantage of these data to separate the Coriolis effects in the Π state, fitting $\beta^{\Pi\Sigma_b}$ and $\beta^{\Pi\Sigma_s}$, the Coriolis coefficients for the Π state interaction with the Σ_b and Σ_s states, respectively. Therefore, it is now possible to analyze the dipole moments from the high quality Stark field data of the LER experiments, leaving the other constants fixed at the values obtained from the zero-field data. This paper reports the results of such an analysis.

Accurate values for the dipole moments and nuclear quadrupole coupling constants are essential to any description of the wave functions for the weakly bound complexes. The generally large vibrational motions are inconsistent with the rigid structures obtained from rotational data alone, and it is often impossible to fix a unique vibrationally averaged geometry based purely on rotational analysis. In the case of ArHCl, the probability density distribution of the Σ_b state is predicted to extend over 40° in θ at half-maximum,⁴ based primarily on the measured dipole and quadrupole coupling constants. [To avoid cumbersome qualifications, however, we will refer to the structure of ArHCl with the bending angle derived from $P_1(\cos \theta)$ as the "molecular geometry."] The b -axis dipole components are angular constants determined by the overlapping regions of two distinct states and therefore can test predicted wave functions at extremes to which $P_1(\cos \theta)$ and $P_2(\cos \theta)$ are less sensitive.

In addition, it is shown below that resolution of these small terms can fix relative signs of the permanent dipole moments. The orientation of one state with respect to another can be obtained from energy contributions from couplings between those states. Second order couplings do not preserve this information, but third order terms involving Coriolis and Stark interactions do allow this determination, if sufficiently resolved.

II. LEAST SQUARES ANALYSIS

Transitions tabulated in the existing literature enabled all the zero-field constants—i.e., all but the dipole moments—to be satisfactorily determined, with the exception of the Σ_s vibrational band origin. This last constant became determinable upon inclusion of recent measurements by the Berkeley group tunable far-infrared laser spectrometer given in Table I. All other transitions used in this work were obtained from the references given above. The data were insufficient for an independent analysis of ArH³⁷Cl, and only ArH³⁵Cl is discussed here. Least squares fitting of the spectroscopic parameters to the transitions used the matrix elements, sign conventions, and algorithm from a recent study of the van der Waals bending states of ArHCN,¹⁴ with the following minor modifications. In much of the far-infrared data, the hyperfine splittings of a given rovibrational transition were more pre-

TABLE I. ArH³⁵Cl $\Sigma_s \leftarrow \Sigma_0$ transition frequencies (MHz) used in this analysis. Multiple assignments for the same frequency indicate unresolved hyperfine structure.

	$F=J+\frac{3}{2}$	$\Delta F=\Delta J$ $F=J+\frac{1}{2}$	$F=J-\frac{1}{2}$	$F=J-\frac{3}{2}$	$F''=J+\frac{3}{2}$	$\Delta F=0$ $F''=J+\frac{1}{2}$	$F''=J-\frac{1}{2}$	$\Delta F=-\Delta J$ $F+J=\frac{3}{2}$
P(5)	953 358.0	953 358.0	953 358.0	953 358.0				
P(4)	957 616.8	957 616.8	957 616.8	957 616.8				
P(2)	965 470.7	965 470.7	965 476.4			965 476.4	965 467.1	
P(1)	969 055.8					969 061.6		969 051.2
R(0)	975 541.3				975 536.2			975 545.4
R(1)	978 437.0	978 437.0	978 430.9		978 431.8	978 441.2		
R(3)	983 557.1	983 557.1	983 557.1	983 555.9	983 551.7	983 559.3	983 561.7	
R(4)	985 789.7	985 789.7	985 789.7	985 789.7	985 784.4	985 791.8	985 794.8	
R(5)	987 810.5							
R(6)	989 626.8							
R(7)	991 239.5							
R(8)	992 654.5							
R(9)	993 873.0							

cise by roughly a factor of 10 than the absolute frequencies. Rather than fitting to several absolute frequencies in these instances, the program fit the constants to one absolute frequency and several hyperfine intervals, allowing the vibrational band origins and hyperfine constants to be determined independently at their appropriate levels of precision. In many cases, hyperfine multiplets were unresolved, in which case, the constants were fit to the arithmetic mean of the calculated component frequencies.

In calculating Stark effect eigenvalues, off-diagonal couplings to $\Delta J = \pm 3$ were included. Stark couplings between the Σ_b and Σ_s states and off-diagonal hyperfine couplings were both found to be insignificant given the experimental precision. The final constants are the result of a simultaneous, weighted fit to all the data. As a result of including the far-infrared data in Table I, the band origin for the Σ_s state is found to lie at 972 414.81(23) MHz, 10 MHz above the value from the LER analysis.¹¹ All other constants obtainable from the zero-field data are comparable to those of Reeve *et al.*¹⁶ and the earlier analyses and are not reported here.¹⁸ Parameter uncertainties were calculated assuming random errors in the experimental measurements. This is presently the only workable assumption, but it may not be wholly appropriate, since the dominant error in some of the LER and tunable far-infrared measurements may be due to systematic frequency shifts of the gas lasers. More carefully calibrated measurements may change the fit constants by slightly more than would be expected from truly statistical errors.

III. RESULTS

In Table II, the excited state dipole moments and standard deviations evaluated for two fits are given. The b -type dipole moments are well-resolved in this analysis, providing a direct measure of the transition strength between these modes and adding to the store of molecular parameters with which to evaluate proposed potential energy surfaces. They are, however, much more poorly determined than the a -type moments, showing that the neglect of the b -type Stark effect in the original LER analyses was rea-

sonable. This is further supported by the agreement between the a -type moments in Table II and those from the earlier work.¹¹⁻¹³

The two fits in Table II correspond to two different sets of signs for the coupling terms. Neglecting the ground state dipole moment, which is not significantly coupled to the excited state constants, the coupling terms consist of two Coriolis constants, two b -axis dipole components, and three a -axis dipole components; hence, seven signs to determine. Two of these may be selected arbitrarily to fix the directions of the a and b axes in the coordinate system. We express the Coriolis coefficients as¹⁴

$$\beta^{\Pi\Sigma} = \frac{\hbar^2}{\sqrt{2}} \langle \psi_{\Pi}(\theta, R) | M^{-1} R^{-2} \frac{\partial}{\partial \theta} | \psi_{\Sigma}(\theta, R) \rangle, \quad (1)$$

where M is the reduced mass of the complex, and the dipole moments are expressed as

$$\mu_a = \mu_{\text{HCl}} \langle \psi(\theta, R) | \cos \theta | \psi(\theta, R) \rangle, \quad (2)$$

$$\mu_b^{\Pi\Sigma} = \mu_{\text{HCl}} \langle \psi_{\Pi}(\theta, R) | \sin \theta | \psi_{\Sigma}(\theta, R) \rangle. \quad (3)$$

Terms dependent on the polarizability of the argon sum to less than 10% of μ_a in all cases and have been neglected in

TABLE II. Dipole moments (in Debye) and product functions N (MHz² D²) and M_r (MHz D²) (see the text) obtained from fits to ArH³⁵Cl data for different average values $\theta_{\text{avg}}^{\Pi}$ of the Ar-Cl-H angle determined from $P_1(\cos \theta)$ for the Π state. The uncertainties are one standard deviation. The standard deviation of the fit normalized to the estimated experimental errors σ_n is given in the last row.

	$\theta_{\text{avg}}^{\Pi} > 90^\circ$	$\theta_{\text{avg}}^{\Pi} < 90^\circ$
μ_{Σ_b}	-0.541 3(11)	-0.530 1(11)
μ_{Π}^a	-0.263 45(29)	0.262 81(37)
$\mu_{\Sigma_s}^a$	0.675 4(36)	0.674 3(45)
$\mu_{\Pi\Sigma_b}^a$	0.365(12)	0.149(12)
$\mu_{\Pi\Sigma_s}^b$	-0.046 5(43)	-0.140 3(64)
N	-49 400	-60 900
M_b	-271	110
M_s	12.7	-38.1
σ_n	0.88	1.10

Eq. (2). The sign of β within a chosen coordinate system depends only on the direction of θ and therefore on the relative directions of the a and b inertial axes. The signs of the a - and b -axis dipole moments, on the other hand, depend only on the directions of their respective reference axes. For example, if the directions of both axes in Fig. 1 are inverted, the dipole moments all change sign, but the signs of the Coriolis coefficients are preserved because the direction of θ remains unchanged. We choose to fix the Coriolis constant $\beta^{\Pi\Sigma_s}$ and the dipole moment $\mu_a^{\Sigma_s}$ positive. This is consistent with previous conventions giving the ground state dipole moment as positive and the assumption that Σ_s must have the same qualitative angular distribution as the ground state. In the present case, because direct coupling between the two excited Σ states is not resolved, the coordinate systems used to describe the two sets of Π - Σ interactions are essentially independent. This means two more signs may be fixed, defining the Π - Σ_b coordinate system, without significantly affecting the outcome of the fit. We choose $\beta^{\Pi\Sigma_b}$ positive and, for consistency with conclusions discussed below, $\mu_a^{\Sigma_b}$ negative. This leaves only three dipole moment signs to determine.

The sensitivity of the fit to the signs of μ_a^{Π} , $\mu_b^{\Pi\Sigma_b}$, and $\mu_b^{\Pi\Sigma_s}$ was tested by fitting these dipole moments under the complete range of signs for their initial values, with the zero-field constants fixed. We define two terms N and M_r , where

$$N = \beta^{\Pi\Sigma_b} \beta^{\Pi\Sigma_s} \mu_b^{\Pi\Sigma_b} \mu_b^{\Pi\Sigma_s} \quad (4)$$

and

$$M_r = \beta^{\Pi\Sigma_s} \mu_b^{\Pi\Sigma_s} \mu_a^{\Pi}, \quad r = b, s. \quad (5)$$

The results are (i) the product N is negative (the fit finds no local minimum otherwise); (ii) the fit converges for both signs of the product M_b , but the standard deviation is slightly better if the value is negative.

With the directions of the a and b axes defined, the action of the operations in Eqs. (1) and (3) is such that the sign of the product $\beta^{\Pi\Sigma_s} \mu_b^{\Pi\Sigma_s}$ is determined by whether the Σ_r state is localized primarily at θ greater than or less than 90° , although the signs of the two individual constants depend on the phase convention arbitrarily chosen for the wave functions. The sign of this product therefore conveys roughly the same information as the sign of $\mu_a^{\Sigma_r}$, but using different criteria—in particular, by convoluting the Σ_r state with the Π state. The sign of the product M_r gives, just as the product $\mu_a^{\Pi} \mu_a^{\Sigma_r}$ would, the relative orientation of the Π and Σ_r states along the a axis, independent of the choice of coordinate system. A negative value implies that the Π and Σ_r states are oriented in the same direction along the a axis.¹⁴ The product $M_b M_s$ always has the same sign as N , and therefore if N is negative, as observed, HCl is in general oriented on opposite sides of $\theta = 90^\circ$ in the two Σ states. Note that this conclusion cannot be drawn from the relative signs of $\mu_a^{\Sigma_b}$ and $\mu_a^{\Sigma_s}$, which are too weakly coupled to each other to impact the fit significantly in this regard.

In Fig. 3, the angular distributions of the Σ_0 , Σ_b , Π ,

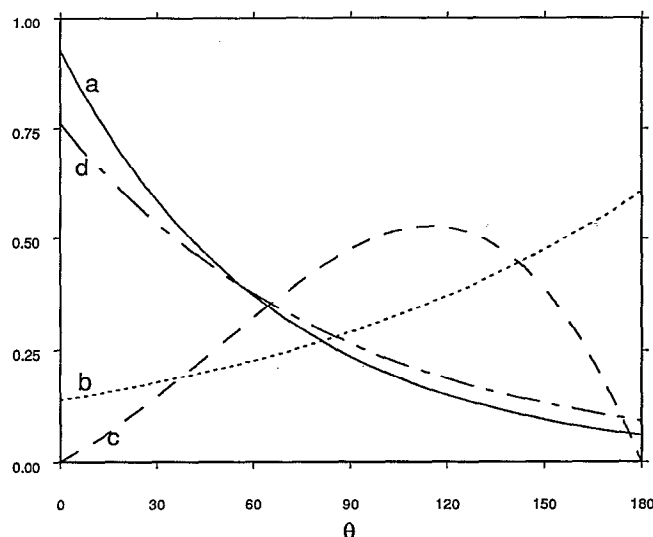


FIG. 3. Estimated angular distributions of HCl in the (a) Σ_0 ground; (b) the Σ_b ; (c) Π ; and (d) Σ_s states. These distributions are based on least squares fits of the dipole and quadrupole constants to a model wave function, as discussed in the text, and are intended only as qualitative descriptions of these states.

and Σ_s state wave functions are represented based on fits of the experimental dipole and quadrupole constants for each state to an assumed Laguerre-type waveform

$$\psi = \exp[-(\theta - \theta_0)/\sigma_\theta] \sin |m|\theta, \quad (6)$$

where θ_0 and σ_θ for each state are the parameters optimized in the fit (except θ_0 was fixed at 0° for the Σ_0 state), and where $|m| = 1$ for the Π state and 0 for the Σ states. The signs for the dipole moments are chosen from the fit results cited in column 2 of Table II.

The two Σ states are shown to have opposite orientations from this analysis, providing experimental verification of a point that has thus far been inferred from the excellent agreement between qualitative features of the observed and predicted rovibrational spectrum.^{3,12} Relative signs of off-diagonal terms in a Hamiltonian matrix are determined only at third order and higher in perturbation theory.¹⁴ The third order term has the form

$$E_n^{21} = \sum_{i \neq n} \sum_{j \neq n} \frac{H_{ni}^a H_{ij}^b H_{jn}^c + H_{ni}^b H_{ij}^c H_{jn}^a + H_{ni}^c H_{ij}^a H_{jn}^b}{(E_n^{00} - E_i^{00})(E_n^{00} - E_j^{00})}, \quad (7)$$

where

$$H_{ij}^a = \langle \Psi_i^{00} | \hat{H}^a | \Psi_j^{00} \rangle. \quad (8)$$

For the present analysis, we allow \hat{H}^a to represent the a -type Stark interaction operator, \hat{H}^b represents the b -type Stark operator, and \hat{H}^c represents the Coriolis coupling operator. In this case, only one term in the numerator in Eq. (7) survives for given states i and j . Choosing the state $n = (\Pi, J=1-)$ as an example, where J is the quantum number for overall rotation of the complex and $+$ or $-$ represents the rotational parity, there are two terms that dominate the third order energy correction

$$E_n^{21} \approx \frac{H_{ni}^a H_{ij}^b H_{jn}^c}{(E_n^{00} - E_i^{00})(E_n^{00} - E_j^{00})} + \frac{H_{ni}^a H_{ni}^b H_{kn}^c}{(E_n^{00} - E_i^{00})(E_n^{00} - E_k^{00})}, \quad (9)$$

where $i = (\Pi, J=1+)$, $j = (\Sigma_b, J=1-)$, $k = (\Sigma_s, J=1-)$, and where

$$H_{ni}^a H_{ij}^b H_{jn}^c \propto \beta^{\Pi\Sigma_b} \mu_b^{\Pi\Sigma_b} \mu_a^{\Pi} = M_b, \quad (10)$$

$$H_{ni}^a H_{ik}^b H_{kn}^c \propto \beta^{\Pi\Sigma_s} \mu_b^{\Pi\Sigma_s} \mu_a^{\Pi} = M_s. \quad (11)$$

The two contributions, proportional to M_b and M_s , are of comparable magnitude—about 50 and 20 MHz, respectively, at 10 kV/cm—because the larger frequency interval $\nu_{\Pi} - \nu_{\Sigma_b}$, compared to $\nu_{\Sigma_s} - \nu_{\Pi}$, is compensated for by the stronger Coriolis and b -type Stark interactions between the two bending states. The signs of these two terms are opposite, M_b and M_s having opposite signs, and they partly cancel. If either of the b -axis dipole components change sign, reversing the sign of one of the M_r terms and implying that the two Σ states are oriented in roughly the same direction, the overall contribution of these terms can be maintained only by reducing the magnitudes of both b -axis components. This is incompatible with second order, non-sign-dependent contributions of these terms to the energy, and evidently does not even correspond to a significant local minimum on the parameter surface. If both terms change sign, as by reversing the sign of μ_a^{Π} from column 2 to column 3 of Table II, the overall contribution to the energy can be roughly maintained if $\mu_b^{\Pi\Sigma_b}$ decreases in magnitude and $\mu_b^{\Pi\Sigma_s}$ increases, as shown.

The preferred orientation of the Π wave function with respect to the b axis is surprising because the semiempirical potentials predict that it should be the opposite.^{3,4} The Π state wave function calculated by Hutson on his H6(3) potential surface⁴ is largely localized on the same side of the b axis as the ground state, and therefore the Σ_s state, although there is substantial amplitude on either side. The difference in standard deviations for the two fits in Table II is small, but note that $\mu_b^{\Pi\Sigma_b}$ and $\mu_b^{\Pi\Sigma_s}$ are of nearly equal magnitude for the column 3 fit. With nearly equal b dipole moments, M_b and M_s differ in magnitude by only a factor of 3, and the Σ_s contribution to the third order correction in Eq. (9) dominates the contribution from the Σ_b because of its lower energy gap. Naively, the couplings between the

stretching and bending states are expected to be substantially weaker than those among the bending states, and this argues in favor of the column 2 constants, giving an Ar-Cl-H angle greater than 90°. The existing data are not sufficiently precise to discriminate further between these fits.

Potential surface analyses that employ these results will therefore have to use the μ_b values appropriate to the Π state orientation chosen. Given the conflicting evidence for the geometry of the Π state, higher precision measurements of these Stark effects would be welcome. Nevertheless, we believe this work demonstrates the high quality of the original LER measurements on this system, as well as the usefulness of detailed spectroscopic analysis in complex coupling problems.

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