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# Laser spectroscopy in a pulsed jet of AIH: Ionization-detected ultraviolet absorption spectra of the transitions $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$ and $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$

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We report the production of radical transients AlH and AlD in a filament-source pulsed freejet expansion. In this source, hydrogen gas from a pulsed valve passes over hot tungsten filament wrapped by a layer of aluminum wire. Liquid aluminum wetting the filament reacts rapidly to form (AlH<sub>3</sub>)<sub>x</sub> oligomer. Depending on filament temperature, either AlH or AlH<sub>2</sub> sublimes from this oligometric coating to be entrained in subsequent pulses of  $H_2$ . The source has been characterized by laser induced fluorescence and ionization-detected onephoton absorption with time-of-flight mass resolution. Laser-induced fluorescence measurements focus on the well-known A-X transition of AlH. Higher energy ionizationdetected absorption spectra resolve the  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transition in AlH and AlD, and for the first time the forbidden transition,  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$ , in AlH. Spectroscopic constants determined from an analysis of bands assigned to v=0 and v=1 of the  $b^{3}\Sigma^{-}$  state are  $T_e = 40524 \text{ cm}^{-1}, B_e = 7.0675 \text{ cm}^{-1}, D_e = 6.1 \times 10^{-5} \text{ cm}^{-1}, \alpha_e = 0.637 \text{ cm}^{-1}, \beta_e = 6.38$ × 10<sup>-4</sup>, and  $\gamma_e = 1.5725$ , with v=0 spin-orbit and spin-rotation coupling parameters  $\lambda_0=0.29$  cm<sup>-1</sup>, and  $\gamma_0=0.03$  cm<sup>-1</sup>, inducing structure in a transition that appears to be predominantly parallel. For v=1, spin-orbit coupling is much stronger, and rotational branch intensities suggest interference, indicating that both parallel and perpendicular components of the transition moment contribute to the total oscillator strength. Results for the C-X (0-0) transitions give  $B_0 = 6.3869 \text{ cm}^{-1}$  and  $D_0 = 5.329 \times 10^{-4}$ with  $T_0 = 44594.05 \text{ cm}^{-1}$  for the AlH C state, and  $B_0 = 3.3457 \text{ cm}^{-1}$  and  $D_0 = 1.380 \times 10^{-4} \text{ cm}^{-1}$  with  $T_0 = 44631.09 \text{ cm}^{-1}$  for the AlD C state.

## I. INTRODUCTION

Metal hydrides have properties that make them important in nuclear engineering, in the purification of metals, and in the preparation of electronically pure metal films, as chemical reducing agents, and for use as high-energy propellants.<sup>1</sup> The abundant hydride, AlH, is a molecule of significance in astrophysics, where its spectrum is found in the emission of sunspots<sup>2</sup> and cooler stars.<sup>3</sup> Such concerns have long stimulated interest in metal-hydrogen bonding, and aluminum hydride, in particular, has been a subject of spectroscopic study for almost a hundred years.<sup>4-15</sup>

Classical studies of the lowest excited singlet state of AlH ( $A^{1}\Pi$ ) in absorption and emission have characterized associated ground and excited state structure in the neighborhood of their potential minima with reasonable precision.<sup>10</sup> More recently, ground state potential parameters have been confirmed by high resolution infrared spectroscopy,<sup>11</sup> and excited-state predissociative lifetimes, obtained by laser-induced fluorescence, have been used to extend the *A*-state potential curve to its dissociation limit.<sup>12</sup>

Knowledge of higher energy states is less secure, despite the growing importance of AlH as a contemporary subject of high-level electronic structure calculations. Transitions from states  $C^{1}\Sigma^{+}$  and  $D^{1}\Sigma^{+}$  to  $X^{1}\Sigma^{+}$  and from  $B^{1}\Sigma^{-}$  to  $A^{1}\Pi$  were first observed some years ago in emission.<sup>5-9,15</sup> Recently, comparable resolution has been achieved in excitation spectra of the C and D states, obtained by ionization-detected two-photon absorption, following laser photolysis of aluminum alkyls.<sup>16</sup> Other work

has assigned excited-state emission from  $b^{3}\Sigma^{-}$  and  $c^{3}\Pi$  to the triplet counterpart of the A state,  $a^{3}\Pi$ .<sup>13,14</sup> These results establish the existence of a rich higher excited-state structure, and raise important questions about absolute positions in the triplet manifold of singly and doubly excited valence and Rydberg configurations.

The electronic structure underlying the spectroscopy of the Group III hydrides is an interesting one. In AlH the  $X^{1}\Sigma^{+}$  state is formed from ground state Al  $3s^{2}3p^{1}$  which supplies a  $3p\sigma$  orbital to overlap H 1s and yield the bonding configuration  $\sigma^{2}$ . The  $A^{1}\Pi$  state, which has configuration  $\sigma\pi$ , is repulsive at large R, mirroring the repulsive interaction between H 1s and the Al 3s valence core when a bonding electron is promoted to the  $3p\pi$  configuration.<sup>17</sup> Bonding at short internuclear distance R results from  $3s^{1}3p^{2}(^{2}D)$  hybridization at Al. The  $C^{1}\Sigma^{+}$  state arises from the higher excited configuration  $3s^{2}4s^{1}(^{2}S)$ , which, at short R, has the form of an  $s\sigma$  Rydberg state built on a  $^{2}\Sigma^{+}$  AlH<sup>+</sup> cation. At long distance, calculations find a deeper outer well dominated by a  $\sigma^{2}$  Al<sup>+</sup>H<sup>-</sup> ionic configuration.<sup>17,18</sup>

In addition to these theoretically well-characterized singlet states, triplet configurations can be predicted and have been investigated in lower-level molecular orbital calculations.<sup>19,20</sup> Chief among these are the  $a^{3}\Pi$  state, which is isoconfigurational with  $A^{1}\Pi$  and computed to lie 12 000 cm<sup>-1</sup> above the ground state. Also considered in these calculations is the important doubly excited  $\pi^{2}$  configuration, which gives rise to the  $b^{3}\Sigma^{-}$  state. As noted above, a transition assigned to originate in this state has been ob-

served in emission to the  $a^{3}\Pi$  state, but, like all the other levels in the triplet manifold, the  $b^{3}\Sigma^{-}$  state has not been well resolved rotationally, and remains unreferenced by experiment to the singlet ground state.

Qualitative molecular orbital pictures of AlH are supported by some of the highest level calculations available for diatomics. Matos, Malmqvist, and Roos<sup>18</sup> have used complete-active space self-consistent-field (CASSCF) methods to study the electronic ground state  $X^{1}\Sigma^{+}$ , first singlet valence state  $A^{1}\Pi$ , and the first Rydberg state  $C^{1}\Sigma^{+}$  of this system. Results are in basic agreement with the early emission spectra. This study also shows that Al 2s and 2p inner-shell correlation has little effect on the spectroscopic constants of these states.

Bauschlicher and Langhoff<sup>17</sup> have taken advantage of this apparent absence of inner-shell correlation to carry out large-scale state-averaged CASSCF calculations with second-order configuration interaction (SOCI) and fullconfiguration interaction (FCI) in which they have succeeded in introducing both important correlation effects and proper Rydberg character in describing variable degrees of valence-Rydberg mixing. The most stringent test in the singlet manifold is, of course, presented by the  $C^{1}\Sigma^{+}$  state, where the authors suggest that AlH calculations serve as a benchmark, from which they will be able to extend optimized methods for describing valence-Rydberg interactions to systems complicated by large dynamic correlations. Unfortunately, it is also the case that the properties of the C state are those most sensitive to the level of theoretical treatment, and, among the observed singlets, those least well characterized by experiment.

We report here new spectroscopic observations which substantially expand the base of available experimental information on the higher excited states of AlH. Our studies make use of a novel method that we have developed for producing a pulsed jet of AlH. We confirm the presence of this diatomic by obtaining the laser-induced fluorescence spectrum of the  $A^{1}\Pi$  state, for which we report improved spectroscopic parameters. Using this source, in conjunction with (1+1) resonant ionization spectroscopy, we present the first rotationally resolved one-photon absorption spectra of the  $C^{1}\Sigma^{+}$  state in AlH and AlD, and, for the first time establish and characterize the direct electronic transition from  $X^{1}\Sigma^{+}$  to  $b^{3}\Sigma^{-}$ .

### II. EXPERIMENTAL METHOD

### A. Experimental apparatus

Excitation spectra of the excited states of AlH are recorded in a free-jet expansion by laser-induced fluorescence (LIF) and mass-resolved one-plus-one resonant ionization spectroscopy. Figure 1 shows an energy-level diagram summarizing energy regions and associated methods. The vacuum system consists of a single chamber comprised of a commercial stainless-steel six-way cross, sealed by Cugasket flanges and evacuated by a liquid-nitrogen trapped 6 in. diffusion pump (Varian VHS-6). A pulsed molecular beam valve (Newport BV-100) enters through the top flange. Interchangeably installed across the axis of the jet



FIG. 1. Energy-level diagram illustrating excitation frequencies and methods for registering absorption: LIF, laser-induced fluorescence; RI, resonant ionization (ionization-detected absorption).

are either the ion optics of a conventional Wily-McClaren time-of-flight (TOF) mass spectrometer, or opposing f1mirror and lens combination, aligned to focus laser excited fluorescence on a filtered photomultiplier (EMI 9558QB). On the other horizontal axis are optical windows for the entrance and exit of the laser beam. For fluorescence experiments, these consist of Brewster-angle windows mounted on 50 cm baffle arms. Mass-filtered ion signal from the TOF microchannel plates or fluorescence signal from the photomultiplier tube is preamplified (Ortec 931) and averaged by a Stanford Research Systems boxcar for digitization on a laboratory microcomputer.

Laser light is provided by either of two systems. For



FIG. 2. Schematic diagram of the tungsten/aluminum filament pulsednozzle source of aluminum hydride. A, 5 mm o.d. alumina tube; B, drilled-through 0.25 in. Cajon Ultra-Torr fitting; C, modified aperture plate; D, Newport BV-100 pulsed molecular beam valve.

laser-induced fluorescence we use a Lambda Physik EMG 202 MSC excimer laser pumping Stilbene 420 dye in a Lambda Physik FL3002 dye laser. For best signal to noise ratio in LIF the laser beam is attenuated to 1  $\mu$ J energy per pulse or less. For (1+1) resonant ionization spectroscopy of higher excited states, the Coumarin 460 output of a Continuum NY-82 Nd:YAG pumped ND-60 dye laser is doubled in BBO. The resulting UV light is passed unfocussed through the extraction region of the TOF mass spectrometer. The laser wavelengths are calibrated by a Burleigh Model 4500 Pulsed Wavemeter, and spectra are corrected to vacuum wave numbers.

#### B. Filament source

The main new instrumental development in this work is the pulsed filament source. Its construction is schematically illustrated in Fig. 2. A 3.2 cm stainless steel aperture plate closing the Newport pulsed valve is fitted with a 0.25 in. i.d. drilled-through Cajon fitting. This fitting holds a 76 mm long by 3 mm i.d. 5 mm o.d. ceramic tube, in contact at one end with the aperture plate, which provides a sealing surface for the viton tip of the valve actuator. Holes drilled 5 and 15 mm from the opposite end of the ceramic tube hold copper connecters that support the filament.

The filament is made by wrapping 0.25 mm tungsten wire with 0.05 mm Al wire. The composite filament is then coiled and inserted in the tube. The filament is heated by the application of current from a dc power supply through an electrical feedthrough in the top flange. The Al wire is observed to melt *in vacuo* and wet the tungsten filament. In our experience, tungsten wire offers superior filament lifetime to tantalum, though both are cited as wetted but not alloyed by molten aluminum.<sup>21</sup>

Jets of AlH or AlD are produced by expanding  $H_2$  or  $D_2$  across the hot filament. Reaction to form aluminum hydride is characterized by the nature of the material deposited from the jet onto a slide held in front of the ceramic tube. Using He as an expansion gas, the valve operating at 10 Hz deposits an aluminum mirror in less than half an hour. Substituting  $H_2$  under the same conditions produces no detectable mirror. We estimate that 80%-90% of the available aluminum is converted to hydride.



FIG. 3. (a) Laser-induced fluorescence spectrum of the  $A^{-1}\Pi - X^{-1}\Sigma^{+}$  transition in AlH. (b) Simulation for a rotational temperature of 650 K using constants listed in Table I, which are derived from a least-squares fit of experimental spectral positions.

Once an experiment is underway, the intensity of the AlH signal becomes rather insensitive to beam parameters such as H<sub>2</sub> backing pressure and gas pulse duration. From this we conclude that AlH is produced by the high-temperature decomposition of  $(AlH_3)_x$  polymer which is formed at the beginning of the heating. Best yields of AlH are obtained by heating the filament at a low temperature (2 V 4–5 A) with a hydrogen flow for 30 min to convert most of aluminum to  $(AlH_3)_x$  polymer, and then increasing the temperature (4 V, 4 A) to decompose  $(AlH_3)_x$  to AlH and which is carried from the nozzle by the expanding hydrogen gas.

The lifetime of the filament is about 3 h for a laserinduced fluorescence experiment, and 5 h for resonant ionization. The pulse width of the gas expansion is about 400  $\mu$ s. For LIF, we install a black anodized 6061-T6 Al tube around the nozzle assembly to shield the PMT from background radiation emitted by the filament.

Typical source conditions are 800 Torr of UHP H<sub>2</sub> or CP D<sub>2</sub> (Matheson) without further purification, 300  $\mu$ m nozzle diameter, 7.5 cm nozzle–laser intersection distance for LIF and 9 cm for MPI, time averaged background pressure nozzle-off,  $1 \times 10^{-7}$  Torr, nozzle-on (10 Hz),  $1 \times 10^{-5}$  Torr.

#### III. RESULTS:

#### A. LIF spectrum of the A-X transition

Figure 3(a) shows the laser-induced fluorescence spectrum of the aluminum hydride jet in the region of 426 nm.





FIG. 4. (a) One-photon resonant two-photon ionization spectrum of the  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transition in AlH. (b) Simulation for a rotational temperature of 650 K using constants listed in Table I, which are derived from a least-squares fit of experimental spectral positions.

Evident here are well resolved P, Q, and R branches. From the work of Zeeman and Ritter,<sup>10</sup> we can immediately recognize this transition as the O-O band of the AlH  $A^{1}\Pi - X^{1}\Sigma^{+}$  system. Based on relative intensity as a function of rotational quantum number, we can estimate a rotational temperature of around 300-400 °C. Variations within the branches reflect excursions in filament temperature over the course of the scan.

# B. Ionization-detected absorption spectra of the C state in AIH and AID

Figure 4 and 5 show one-plus-one resonance-enhanced ionization spectra of AlH and AlD in the region from 44 300 to 44 800 cm<sup>-1</sup>. Conventional emission spectra place  $T_0$  for the C-X transition in AlH at 44 598.66 cm<sup>-1.6,15,22</sup> This agrees reasonably with the band center at 44 594.05 cm<sup>-1</sup> for the system in Fig. 4, which suggests that these two strong spectra correspond to the classical systems assigned some time ago as the  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transitions of AlH and AlD. Both spectra show the rotational structure expected for a one-photon  ${}^{1}\Sigma^{+}-{}^{1}\Sigma^{+}$  transition, with well resolved P and R branches, and no Q branch.

# C. Ionization-detected absorption spectra of the $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$ transition in AIH

Figures 6 and 7 show (1+1) ionization spectra of AlH taken from scans beginning about 3000 cm<sup>-1</sup> to the red of the C state. Surprisingly, we find bands in this region that feature structured Q branches, accompanied by well-

FIG. 5. (a) One-photon resonant two-photon ionization spectrum of the  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transition in AlD. (b) Simulation for a rotational temperature of 650 K using constants listed in Table I, which are derived from a least-squares fit of experimental spectral positions.

resolved progressions to the red and blue, spaced by approximately  $24 \text{ cm}^{-1}$ . In none of its excited states does the AlH bond distance provide for a rotational constant larger than 6-7 cm<sup>-1</sup>, which means that P- and R-branch spacings should be no greater than 14  $cm^{-1}$ . Therefore, the transitions we see here must be following rotational selection rules of  $\Delta N=0, \pm 2$ . Such selection rules can arise in single-photon  $\Sigma^+ - \Sigma^-$  transitions induced by spin-orbit coupling. As noted above, indirect experimental observations<sup>13,14</sup> together with molecular orbital calculations<sup>19,20</sup> place the  $\pi^2 b^3 \Sigma^-$  state of AlH at about this energy. Rotational analysis discussed below confirms this suggestion, and allows us to assign these band systems to ionizationdetected absorption in the direct transition from  $X^{1}\Sigma^{+}$  to successive vibrational levels of  $b^{3}\Sigma^{-}$ . We detect no intensity for corresponding transitions in AlD.

## **IV. DISCUSSION**

# A. The $A^{1}\Pi$ state

The signal-to-noise ratio and resolution are improved in the laser-induced-fluorescence spectrum of Fig. 3 compared with early emission results, and thus it is worthwhile to reanalyze the structure of the  $A^{1}\Pi$  state to obtain more accurate spectroscopic constants. For this purpose, we perform a least-squares fit of positions across the spectrum to the upper-state Hamiltonian:

$$E_{v}(J) = B_{v}J(J+1) - D_{v}J^{2}(J+1)^{2} \pm [A_{0} + A_{1}J(J+1)],$$
(1)



FIG. 6. (a) One-photon resonant two-photon ionization spectrum of the  $(0-0) b^3 \Sigma^- - X^1 \Sigma^+$  transition in AlH. (b) Simulation for a rotational temperature of 650 K using constants listed in Table I, which are derived from a least-squares fit of experimental spectral positions, assuming that the Q branch is dominated by its  ${}^{Q}P + {}^{Q}R$  components. Intensities are determined by the product of 650 K Boltzmann population and rotational linestrength factors (cf. Table V), assuming that the perpendicular transition moment is zero.

which includes terms  $A_0$  and  $A_1$  to account for  $\Lambda$ -doubling resolved in Q(J) - P(J+1) and R(J-1) - Q(J) combination differences.

Constants derived from the fit are collected in Table I. The line-for-line match with residuals is listed in Table II. A simulation based on derived parameters is pictured in Fig. 3(b).

In its principal constants, our rotational analysis of the  $A^{1}\Pi - X^{1}\Sigma^{+}$  transition differs only slightly from the results of Zeeman and Ritter.<sup>10</sup> However, we find that inclusion of  $\Lambda$ -doubling parameters reduces the average residual by more than a factor of 4.

# B. The C ${}^{1}\Sigma^{+}$ state

As noted above, the C state of aluminum hydride is derived from the Al  $3s^24s^1$  (<sup>2</sup>S) state. Theory suggests that it has a double-well potential, which is primarily Rydberg in character for small R.<sup>17,18</sup> The  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transition is dipole allowed, and was first reported in emission more than 60 years ago,<sup>6</sup> but uncertainties exist in these early assignments. Absolute frequencies disagree, and at least one author notes two transition systems overlapping in this region.<sup>6-9</sup>

Rotational structure is well-resolved in both spectra, and we are easily able to apply our least-squares fitting routines to the full set of spectral positions for AlH and AlD in Figs. 4 and 5. The resulting constants are presented in Table I. Experimental positions of all the lines are compared with calculated ones in Tables III and IV. Experimental spectra are accompanied in both cases by simulations based on the respective fits.

For both AlH and AlD, the laser spectroscopic results provide a solid confirmation of the rotational structure derived from the early emission data. New constants  $B_0$ = 6.3869 and 3.3457 cm<sup>-1</sup> agree remarkably with old estimates, 6.393 and 3.35 cm<sup>-1</sup> respectively. However, as already noted, we find  $T_0$  for both bands 3–5 cm<sup>-1</sup> to the red of their spectrographic placement.<sup>8,15,22</sup>

## C. The $b^{3}\Sigma^{-}$ state

### 1. Rotational structure

 ${}^{3}\Sigma^{--1}\Sigma^{+}$  transitions have been observed in a number of small molecules, including N<sub>2</sub> (B'  ${}^{3}\Sigma_{u}^{-}-X^{1}\Sigma_{g}^{+}$ ),<sup>23</sup> NH (b  ${}^{1}\Sigma^{+}-X^{3}\Sigma^{-}$ ),<sup>24</sup> NF (b  ${}^{1}\Sigma^{+}-X^{3}\Sigma^{-}$ ),<sup>25</sup> CO ( $e^{3}\Sigma^{-}-X^{1}\Sigma^{+}$ ),<sup>26</sup> and CO<sub>2</sub> ( $\pi_{g}^{3}3p\pi_{u}^{-}3\Sigma_{u}^{-}-X^{1}\Sigma_{g}^{+}$ ),<sup>27</sup> Spectra are generally characterized by a strong and congested Q branch, on either side of which are found  ${}^{5}R$  and  ${}^{O}P$  branches ( $\Delta N = \pm 2$ ) with spacings of about 6B<sub>v</sub> from



FIG. 7. (a) One-photon resonant two-photon ionization spectrum of the  $(1-0) \dot{b}{}^{3}\Sigma^{-}-X{}^{1}\Sigma^{+}$  transition in AlH. (b) Simulation for a rotational temperature of 650 K using constants listed in Table I, which are derived from a least-squares fit of experimental spectral positions which includes the  $^{2}Q$  branch. Intensities are determined by the product of 650 K Boltzmann population and rotational linestrength factors (cf. Table V), assuming a perpendicular to parallel transition moment ratio of 1.2. Bands comparable to Fig. 6 (0-0) and Fig. 7 (1-0) have not been found in the AlD spectrum.

the band origin to the first line of each branch and subsequent spacings of  $4B_v$  between each rotational line.

Watson,<sup>28</sup> Hougen,<sup>29</sup> and Lefebvre-Brion and Field<sup>30</sup> have detailed the calculation of rotational wave functions and transition moments for  ${}^{3}\Sigma^{-}$  states. As opposed to the first-row examples cited above, we anticipate that the  $\lambda$ value pertaining to the splitting of  $\Omega$  components may be large in heavier AlH. If such is the case, its most obvious manifestation in the spectrum will be a displacement of the first members of the  ${}^{S}R$  and  ${}^{O}P$  branches away from a symmetrical  $6B_{v}$  spacing about the origin. To conduct a complete rotational analysis of the AlH  ${}^{3}\Sigma^{-1}\Sigma^{+}$  transition, we use the following Hamiltonian for J=N, J=N-1, and J=N+1 rotational levels  $(J \ge 1)$ :

$$BN(N+1) - D[N(N+1)]^2,$$
 (2)

$$BN(N+1) - B(2N-1) - \lambda$$
  
+  $[\lambda^2 - 2B\lambda + B^2(2N-1)^2]^{1/2} - \gamma N + \frac{1}{2}\gamma$   
-  $D[N(N+1)]^2,$  (3)  
$$BN(N+1) + B(2N+3) = \lambda$$

TABLE I. Rotational constants obtained by least-squares fits of experimental positions listed in Tables II, III, IV, V, and VI for spectra assigned to AlH and AlD A, C, and b states

Term	$\frac{T_0}{(\mathrm{cm}^{-1})}$	$B_v$ (cm <sup>-1</sup> )	$\frac{D_v}{(cm^{-1}) \times 10^{-4}}$	$A_0$ (cm <sup>-1</sup> )×10 <sup>-3</sup>	$A_1$ (cm <sup>-1</sup> )×10 <sup>-3</sup>	$\lambda$ (cm <sup>-1</sup> )	$\gamma$ (cm <sup>-1</sup> )
$1\Sigma + (AlH)$	0	6.2978	3.565				
$A^{i}\Pi$ (AlH)	23 470.54	6.0209	6.600	1.61	3.81		
$C^{1}\Sigma^{+}$ (AlH)	44 594.05	6.3870	5.304				
$C^{1}\Sigma^{+}$ (AlD)	44 631.09	3.3457	1.380				
$b^{3}\Sigma^{-}$ (AlH) v=0	41 774.43	6.7546	3.977			0.26	0.10
$b^{3}\Sigma^{-}$ (AlH) v=1	43 688.51	6.1120	10.15			12.02	0.226

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TABLE II. Experimental positions observed for the band system in AlH assigned to the  $A^{1}\Pi - X^{1}\Sigma^{+}$  (0-0) transition, compared with those calculated from the rotational constants given in Table I which were determined by a least-squares fit to the spectrum.

<b>FABLE III.</b> Experimental positions observed for the band system in AlH
assigned to the $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$ transition, compared with those calculated
rom the rotational constants given in Table I which were determined by
a least-squares fit to the spectrum.

	$\omega_{\rm obs}$	$\omega_{\rm calc}$	$\omega_{\rm obs} - \omega_{\rm calc}$
Transition	$(cm^{-1})$	$(cm^{-1})$	$(cm^{-1})$
		02.444.00	0.15
P(2)	23 444.97	23 444.82	0.15
P(3)	23 431.20	23 431.14	0.06
<i>P</i> (4)	23 416.84	23 416.93	-0.09
P(5)	23 402.02	23 402.16	-0.14
<i>P</i> (6)	23 386.86	23 386.81	0.05
P(7)	23 371.05	23 370.85	0.20
P(8)	23 354.19	23 354.25	-0.06
P(9)	23 336.85	23 336.96	-0.11
P(10)	23 319.00	23 318.94	0.06
P(11)	23 300.37	23 300.13	0.24
P(12)	23 280.46	23 280.45	0.01
P(13)	23 259.88	23 259.85	0.03
P(14)	23 238.60	23 238.23	0.37
P(15)	23 215.51	23 215.52	-0.01
O(1)	23 469.94	23 469.97	-0.03
$\tilde{O}(2)$	23 468.76	23 468.84	-0.08
Q(3)	23 467.02	23 467.12	-0.10
$\tilde{O}(4)$	23 464 74	23 464 80	-0.06
O(5)	23 461 84	23 461 84	0.00
Q(5)	23 458 17	23 458 21	_0.00
Q(0)	23 453 88	23 453 86	0.07
Q(7)	23 433.88	23 433.00	0.02
Q(0)	23 440.07	23 440.74	0.15
Q(9)	23 442.90	23 442.79	0.11
$\mathcal{Q}(10)$	23 430.03	23 433.93	0.10
Q(11)	23 428.13	23 428.14	-0.01
Q(12)	23 419.27	23 419.29	-0.02
Q(13)	23 409.23	23 409.30	-0.07
Q(14)	23 398.04	23 398.07	-0.03
Q(15)	23 385.50	23 385.52	-0.02
R(0)	23 482.41	23 482.59	-0.18
R(1)	23 494.02	23 494.07	-0.05
R(2)	23 505.02	23 504.97	0.05
R(3)	23 515.45	23 515.25	0.20
R(4)	23 525.00	23 524.88	0.12
R(5)	23 533.75	23 533.80	-0.05
R(6)	23 541.85	23 541.97	-0.12
<b>R</b> (7)	23 549.15	23 549.33	-0.18
R(8)	23 555.56	23 555.81	-0.25
R(9)	23 561.18	23 561.34	-0.16
R(10)	23 565.74	23 565.82	-0.08
R(11)	23 569.10	23 569.19	-0.09
R(12)	23 571.30	23 571.33	-0.03
R(13)	23 572.05	23 572.14	-0.09

$$-[\lambda^{2}-2B\lambda+B^{2}(2N+3)^{2}]^{1/2}+\gamma(N+1)+\frac{1}{2}\gamma$$
$$-D[N(N+1)]^{2}.$$
 (4)

Five rotational branches are optically allowed. These are  ${}^{S}R$ ,  ${}^{Q}R$ ,  ${}^{Q}Q$ ,  ${}^{Q}P$ , and  ${}^{O}P$ . As can be seen from the linestrength formulas summarized in Table V, the intensities of the P and R branches depend on the magnitudes and relative signs of both parallel and perpendicular components of the transition moment. Thus absorption in either the ( ${}^{S}R$ ,  ${}^{O}P$ ) or ( ${}^{Q}R$ ,  ${}^{Q}P$ ) pairs can be reduced to zero by interference. The intensity of the  ${}^{Q}Q$  branch depends on  $\mu_1$  alone.

Transition	$\omega_{obs}$ (cm <sup>-1</sup> )	$\omega_{calc}$ (cm <sup>-1</sup> )	$\omega_{\rm obs} - \omega_{\rm calc}$ (cm <sup>-1</sup> )	
P(1) 44 581.45		44 581.46	-0.01	
P(2)	44 569.36	44 569.05	0.31	
P(3)	44 557.07	44 556.83	0.24	
<i>P</i> (4)	44 544.71	44 544.80	0.09	
P(5)	44 532.99	44 532.96	0.03	
P(6)	44 521.45	44 521.30	0.15	
P(7)	44 510.13	44 509.80	0.33	
P(8)	44 498.70	44 498.45	0.25	
P(9)	44 487.48	44 487.23	0.25	
<b>P</b> (10)	44 475.74	44 476.11	0.37	
P(11)	44 464.49	44 465.06	-0.57	
P(12)	44 453.73	44 454.06	-0.33	
P(13)	44 442.97	44 443.04	-0.07	
P(14)	44 432.40	44 432.00	0.40	
P(15)	44 420.95	44 420.86	0.09	
<b>R</b> (0)	44 606.49	44 606.82	-0.33	
R(1)	44 619.73	44 619.76	-0.03	
R(2)	44 632.83	44 632.84	0.01	
R(3)	44 646.21	44 646.05	0.16	
R(4)	44 659.48	44 659.36	0.12	
R(5)	44 672.81	44 672.75	0.06	
R(6)	44 686.35	44 686.17	0.18	
R(7)	44 699.69	44 699.59	0.10	
R(8)	44 712.95	44 712.96	-0.01	
R(9)	44 726.30	44 726.45	-0.15	
<b>R</b> (10)	44 739.30	44 739.39	-0.09	
<b>R</b> (11)	44 752.40	44 752.34	0.08	
R(12)	44 765.06	44 765.03	0.03	
R(13)	44 777.29	44 777.40	-0.11	

Inspection of the first band in the  ${}^{3}\Sigma^{-}-{}^{1}\Sigma^{+}$  transition system (Fig. 6) shows a red-shaded Q branch symmetrically placed between clear progressions of  ${}^{S}R$  and  ${}^{O}P$  lines. Using literature values for the X state rotational constants,<sup>22</sup> we optimize rotational parameters for this band by a least-squares fit of the above Hamiltonian to the spectral positions. For the small value of  $\lambda$  returned by this fitting procedure (0.26), the  ${}^{Q}Q$  and  ${}^{Q}P + {}^{Q}R$  branches are nearly degenerate. Thus the Q branch could be assigned to either  ${}^{Q}O$  or  ${}^{Q}P + {}^{Q}R$  or both. A clear distinction cannot be made on the basis of present experimental resolution, but we find slightly smaller deviations in the Q branch by fitting the spectrum in this case to the Hamiltonian for  $^{Q}P + ^{Q}R$  alone. Table VI compares experimental line positions with ones calculated from the parameters of such a fit. Figure 8(a) shows an expanded view of the Q branch detailing the correspondence between features of the experimental spectrum and ladders of calculated  $\Delta J=0$  positions.

Linestrength expressions clearly show the effect of interference in  ${}^{3}\Sigma^{-}-{}^{1}\Sigma^{+}$  transitions:  $({}^{S}R, {}^{O}P)$  and  $({}^{Q}R, {}^{Q}P)$ branches cannot both be strong when parallel and perpendicular transition moments have comparable magnitudes. Therefore, our suggestion of a strong  ${}^{Q}P + {}^{Q}R$  branch in this spectrum implies substantially different magnitudes for

TABLE IV. Experimental positions observed for the band system in AlD assigned to the  $C^{1}\Sigma^{+}-X^{1}\Sigma^{+}$  transition, compared with those calculated from the rotational constants given in Table I which were determined by a least-squares fit to the spectrum.

TABLE VI. Experimental positions observed for the band system in AlH
assigned to the $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$ (0-0) transition, compared with those cal-
culated from the rotational constants given in Table I which were deter-
mined by a least-squares fit to the spectrum. <sup>a</sup>

Transition	$(\mathrm{cm}^{-1})$	$\omega_{calc}$ (cm <sup>-1</sup> )	$\omega_{obs} - \omega_{calc}$ (cm <sup>-1</sup> )	
P(1)	P(1) 44 624.33		-0.19	
P(2)	44 617.75	44 618.08	-0.33	
P(3)	44 611.66	44 611.77	-0.11	
<i>P</i> (4)	44 605.57	44 605.58	-0.01	
P(5)	44 599.38	44 599.52	-0.14	
P(6)	44 593.49	44 593.59	-0.10	
P(7)	44 587.70	44 587.77	0.07	
P(8)	44 582.00	44 582.09	-0.09	
P(9)	44 576.51	44 576.51	0.00	
P(10)	44 570.94	44 571.04	-0.20	
P(11)	44 565.63	44 565.67	-0.04	
P(12)	44 560.32	44 560.41	-0.09	
P(13)	44 555.19	44 555.22	-0.01	
P(14)	44 550.65	44 550.12	0.53	
P(15)	44 545.11	44 545.07	0.04	
P(16)	44 540.16	44 540.09	0.07	
P(17)	44 535.22	44 535.15	0.07	
P(18)	44 530.18	44 530.24	-0.06	
<b>R</b> (0)	44 637.85	44 637.78	0.07	
<b>R</b> (1)	44 644.51	44 644.59	-0.08	
R(2)	44 651.46	44 651.52	-0.06	
R(3)	44 658.22	44 658.55	-0.33	
R(4)	44 665.75	44 665.70	0.05	
R(5)	44 672.90	44 672.94	-0.04	
R(6)	44 680.04	44 680.27	-0.23	
R(7)	44 687.38	44 687.68	-0.30	
R(8)	44 695.10	44 695.15	-0.05	
R(9)	44 702.38	44 702.69	-0.31	
<b>R</b> (10)	44 710.35	44 710.27	0.08	
<b>R</b> (11)	44 717.89	44 717.89	0.00	
R(12)	44 725.57	44 725.52	0.05	
R(13)	44 733.33	44 733.16	0.17	
R(14)	44 740.90	44 740.79	0.11	
R(15)	44 748.42	44 748.38	0.04	
<b>R</b> (16)	44 755.97	44 755.93	0.04	
R(17)	44 763.28	44 763.42	-0.14	
<b>R</b> (18)	44 770.69	44 770.81	-0.12	

 $\mu_{\parallel}$  and  $\mu_{\perp}$ . Experimental signs point to a predominantly parallel transition. Choosing  $\mu_{\perp}$  to be the larger predicts a much greater overall *Q*-branch intensity than we observe experimentally. Our presumption above of a weak  ${}^{Q}Q$  com-

TABLE V. Rotational linestrength formulas for  ${}^{3}\Sigma^{-}-{}^{1}\Sigma^{+}$  transitions in the Hund's case (b) (small  $\lambda$ ) limit.

Transition	J	Relative linestrength <sup>a</sup>
<sup>0</sup> P(N)	N-1	$[\mu_{\parallel} + \mu_{\perp}]^2 J (J-1) / (2J-1)$
$Q_{P(N)}$	N+1	$[(J)\mu_{\parallel} - (J-1)\mu_{\perp}]^2/(2J-1)$
Q(N)	N	$[\mu_1]^2(2J+3)$
$Q_{R(N)}$	N - 1	$[(J+1)\mu_{\parallel} - (J+2)\mu_{\perp}]^2/(2J+3)$
SR(N)	N+1	$[\mu_{\parallel} + \mu_{\perp}]^{2}(J+1)(J+2)/(2J+3)$

<sup>a</sup>Formulation advanced by Watson (Ref. 28) and Hougen (Ref. 29), and summarized by Lefevbre-Brion and Field (Ref. 30). Hougen's notation is used to define  $\mu_{\parallel}$  and  $\mu_1$ . To convert to Watson's notation, substitute  $\mu_0$  for  $\mu_{\parallel}$  and  $-\mu_1$  for  $\mu_1$ .

Transition	Transition $(cm^{-1})$		$\omega_{obs} - \omega_{calc}$ (cm <sup>-1</sup> )	
<sup>0</sup> P(2)	41 736.29	41 736.53	-0.24	
<sup>o</sup> P(3)	41 712.23	41 712.28	-0.05	
$O_P(4)$	41 688.94	41 689.01	-0.07	
$^{O}P(5)$	41 666.81	41 666.72	0.09	
$O_P(6)$	41 645.41	41 645.41	0.00	
OP(7)	41 625.33	41 625.11	0.22	
OP(8)	41 605.93	41 605.81	0.12	
OP(9)	41 587.69	41 587.54	0.15	
$^{o}P(10)$	41 570.38 41 553.74	41 570.29	-0.35	
$Q_{R(0)}$		41 774.30		
$Q_{P(1)}$	41 774.96	41 774.81	0.15	
$Q_R(1)$		41 775.21		
$^{Q}Q(1)$		41 775.34		
$Q_{P(2)}$	41 776.72	41 776.78	-0.06	
$Q_R(2)$		41 777.05		
Q(2)		41 777.17		
$\mathcal{Q}P(3)$	41 779.58	41 779.52	0.06	
$\mathcal{L}_{\mathcal{R}(3)}^{\mathcal{L}}$		41 779.81		
$\mathcal{L}_{Q(3)}$	41 702 14	41 7/9.91	0.01	
$\mathcal{P}(4)$	41 /83.14	41 783.13	-0.01	
$Q_{O(4)}$		41 783 55		
$Q_{P(5)}$	41 787 63	41 787 67	_0.04	
$Q_{R(5)}$	41 /07.05	41 788.05	-0.04	
$Q_{O(5)}$		41 787.10		
$Q_{P(6)}$	41 792.95	41 793.09	-0.14	
$Q_{R(6)}$		41 793.52		
Q(6)		41 793.54		
$Q_{P(7)}$	41 799.25	41 799.41	-0.16	
$Q_R(7)$		41 799.89		
Q(7)		41 799.88		
QP(8)	41 806.45	41 806.60	-0.15	
$\mathcal{Q}_{R(8)}$		41 807.14		
2Q(8)	41 014 26	41 807.11	0.39	
$\mathcal{P}(9)$	41 814.30	41 814.08	-0.28	
$Q_{\Omega(9)}$		41 015.20		
$Q_{P(10)}$	41 823 37	41 823 62	0.25	
$Q_R(10)$	11 020101	41 824.28	0.20	
<sup>Q</sup> O(10)		41 824.18		
$\widetilde{Q_{P(11)}}$	41 833.09	41 833.42	-0.33	
$Q_{R(11)}$		41 834.13		
<sup>Q</sup> Q(11)		41 834.01		
$s_{R(0)}$	41 814.33	41 814.55	-0.22	
SR(1)	41 842.26	41 842.45	-0.19	
SR(2)	41 870.95	41 871.19	-0.24	
$^{S}R(3)$	41 900.95	41 900.76	0.19	
<sup>3</sup> R(4)	41 931.21	41 931.16	0.05	
~K(5) SR(C)	41 962.50	41 962.35	0.15	
-K(0) Sp(7)	41 994.70	41 994.52	0.38	
-K(/) Sp(9)	42 027.40	42 027.03	0.43	
SP(0)	42 000.77	42 000.47	0.30	
SR(10)	42 094.70	42 074.01	0.15	
$s_{R(11)}$	42 127.37	42 127.41	_0.10	
A(11)	42 104.00	42 104.0J	-0.05	

<sup>a</sup>The Hamiltonian [Eqs. (2)-(4)] is fit to  ${}^{O}P$ ,  ${}^{Q}P$  +  ${}^{Q}R$ , and  ${}^{S}R$  branches only. The perpendicular transition moment,  $\mu_1$ , is assumed to be nearly zero for the (0-0) band on the basis of this slightly better fit of experimental Q-branch positions to the  ${}^{Q}P$  +  ${}^{Q}R$  satellite branch alone as opposed to one fitting the  ${}^{Q}Q$  branch alone. If we make the alternative assumption that the (0-0) transition is purely perpendicular instead of parallel, then all three components are allowed. In that case an acceptable fit is achieved, but the Q branch is predicted to be far more intense than observed experimentally.

TABLE VII. Experimental positions observed for the band system in AlH assigned to the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  (1-0) transition, compared with those calculated from the rotational constants given in Table I which were determined by a least-squares fit to the spectrum.<sup>a</sup>

Transition	$(\mathrm{cm}^{-1})$	$(\mathrm{cm}^{-1})$	$\omega_{obs} - \omega_{calc}$ (cm <sup>-1</sup> )	
<sup>0</sup> P(2)	43 639.42	43 639.11	0.31	
$o_{P(3)}$	43 613.78	43 613.78	0.00	
<sup>o</sup> P(4)	43 588.13	43 588.11	0.02	
<sup>0</sup> P(5)	43 562.36	43 562.09	0.27	
<i><sup>0</sup>P</i> (6)	43 536.00	43 535.72	0.28	
<sup>0</sup> P(7)	43 509.29	43 508.82	0.47	
<sup>0</sup> P(8)	43 481.80	43 481.47	0.33	
<sup>0</sup> P(9)	43 453.78	43 453.54	0.24	
<sup>0</sup> P(10)	43 424.98	43 424.93	0.05	
<sup>0</sup> P(11)	43 395.37	43 395.54	-0.17	
<sup>Q</sup> Q(1)	43 688.41	43 688.14	0.27	
$Q_R(0)$		43 676.89		
$Q_R(1)$		43 676.71		
$Q_P(1)$		43 675.80		
$^{Q}Q(2)$	43 687.82	43 687.37	0.45	
$Q_R(2)$		43 676.15		
<sup>Q</sup> P(2)		43 674.95		
Q(3)	43 686.59	43 686.18	0.41	
$Q_R(3)$		43 675.18		
$Q_{P(3)}$		43 673.57		
<sup>Q</sup> Q(4)	43 684.71	43 684.53	0.18	
$Q_R(4)$		43 673.74		
$Q_P(4)$		43 671.71		
QQ(5)	43 682.44	43 682.34	0.10	
$Q_R(5)$		43 671.77		
$Q_P(5)$		43 669.30		
$Q_Q(6)$	43 679.47	43 679.54	-0.07	
$Q_R(6)$		43 669.18		
QP(6)		43 666.29		
Q(7)	43 675.86	43 676.03	-0.17	
$Q_R(7)$		43 665.89		
$\nabla P(7)$		43 662.56		
Q(8)	43 671.46	43 671.70	-0.24	
$\mathcal{L}_{\mathcal{R}(\delta)}$		43 661.78		
P(8)	12 ((( 12	43 658.02	0.21	
$\frac{2}{2}(9)$	43 000.12	43 000.43	-0.31	
$\mathcal{L}_{\mathcal{R}}(\mathbf{y})$		43 030.73		
<sup>-</sup> r(9)	42 650 92	43 032.33	0.25	
$Q_{P(10)}^{-Q(10)}$	45 057.82	43 650 50	-0.25	
$Q_{P(10)}$		43 645 94		
<i>Q</i> (11)	43 652 08	43 652 46	0.38	
$Q_{R(11)}$	10 002100	43 643.20	0.50	
$Q_{P(11)}$		43 638.12		
Q(12)	43 643.19	43 643.43	-0.24	
$Q_{R(12)}$		43 634.38		
$Q_{P(12)}$		43 628.87		
<sup>Q</sup> Q(13)	43 632.57	43 632.78	-0.21	
$Q_{R}(13)$		43 623.96		
<i>QP</i> (13)		43 618.00		
<sup>S</sup> R(0)	43 711.71	43 712.68	-0.97	
$s_{R(1)}$	43 735.54	43 736.43	-0.89	
SR(2)	43 758.71	43 759.64	-0.93	
SR(3)	43 781.33	43 782.26	-0.93	
SR(4)	43 803.57	43 804.19	0.62	
SR(5)	43 824.96	43 825.31	0.35	
SR(6)	43 845.86	43 845.50	0.36	
SR(7)	43 865.77	43 864.61	0.99	
<sup>3</sup> R(8)	43 884.68	43 882.49	2.19	

<sup>a</sup>The Hamiltonian [Eqs. (2)-(4)] is fit to  ${}^{O}P$ ,  ${}^{O}Q$ , and  ${}^{S}R$  branches only. The ratio,  $\mu_1/\mu_{\parallel}$  is estimated from a qualitative fit to intensities. At the resulting perpendicular to parallel transition moment ratio of 1.2, calculated intensities of  ${}^{O}P$  and  ${}^{R}R$  branches are too small for their spectra to be discernible in simulations. Structure assignable to these branches cannot be detected in the experimental spectrum.



FIG. 8. (a) Expanded view taken from Fig. 6 showing the central (*Q*-branch) portion of the one-photon resonant two-photon ionization spectrum of the (0-0) band of the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition in AlH. (b) Expanded view taken from Fig. 7 showing the central (*Q*-branch) portion of the one-photon resonant two-photon ionization spectrum of the (1-0) band of the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition in AlH.

ponent is also consistent with the idea that  $\mu_1$  is the smaller transition moment. We emphasize again, however, that current experimental resolution does not cleanly separate the components of the Q branch for this band, so that conclusions about the relative magnitudes of its perpendicular versus parallel transition moments must be regarded as provisional.

Figure 7 shows a significantly different situation for the second band of the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition system. Here we see a blue-shaded Q branch, asymmetrically placed between strong SR and OP branches. Least-squares fitting confirms a much larger  $\lambda$  (12.02). At this value of  $\lambda$ , the  ${}^{Q}Q$  branch is well separated from  ${}^{Q}P + {}^{Q}R$ . As can be seen from the ladders in Fig. 7, and confirmed by comparing observed and calculated frequencies in Table VII, observed transitions in the Q branch of the second band can be assigned entirely to  ${}^{Q}Q$ , with no detectable intensity in the satellites. Figure 8(b) offers a higher-resolution view of the correspondence between features in the experimental spectrum and the ladder of calculated  ${}^{Q}Q$  positions. From this result, we can immediately conclude that, in addition to a large  $\lambda$ , the higher-energy band of the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition can be characterized by a perpendicular transition moment of comparable magnitude to  $\mu_{\parallel}$ , and of a relative

TABLE VIII. Equilibrium rovibrational parameters derived from spectroscopic data associated with ionization detected absorption transitions from  $X^{1}\Sigma^{+}$  (v=0) to the v=0 and v=1 levels of  $b^{3}\Sigma^{-}$ .

$\frac{T_e^{a}}{(\mathrm{cm}^{-1})}$	$B_e$ (cm <sup>-1</sup> )	$D_e$ (cm <sup>-1</sup> )	$lpha_e$ (cm <sup>-1</sup> )	$\beta_e$ (cm <sup>-1</sup> )	<i>r<sub>e</sub></i> (Å)	$\omega_e x_e^{a}$ (cm <sup>-1</sup> )	$\omega_e^a$ (cm <sup>-1</sup> )
41 445	7.0759	0.89×10 <sup>-4</sup>	0.643	6.17×10 <sup>-4</sup>	1.5717	275	2464

<sup>a</sup>Estimated from experimentally determined  $B_e$ ,  $\alpha_e$ ,  $\omega_e$  and  $\omega_e x_e$ , assuming the potential of  $b^{3}\Sigma^{-}$  fits a Morse function [cf. Eq (5)].

sign appropriate for interference in the  ${}^{Q}P + {}^{Q}R$  branch. Fitting experimental intensities to simulated ones, we estimate  $\mu_{\parallel}/\mu_{\perp}$  for the higher-energy band to be +1.2, using the phase convention of Hougen<sup>29</sup> (cf. Table V).

Spectral parameters obtained by least-squares fits to both band systems are summarized in Table I. Figures 6(b) and 7(b) show simulated spectra for each band as reconstructed from their respective fits using the linestrength formulas for  ${}^{3}\Sigma^{-}-{}^{1}\Sigma^{+}$  transitions in conjunction with the respective assumptions stated above for the magnitude and sign of  $\mu_{\parallel}$  relative to  $\mu_{\perp}$ .

### 2. Vibrational parameters

The origins derived for these two band systems are separated by about 1900 cm<sup>-1</sup>, or the order of one quantum of AlH vibration. The rotational constant obtained by fit to the lower energy, 41 774 cm<sup>-1</sup>, band system is 6.7546 cm<sup>-1</sup>, which matches reasonably with the value estimated for v=0 of the  $b^{3}\Sigma^{-}$  state from the emission spectrum of the  $b^{3}\Sigma^{-}-a^{3}\Pi$  transition. The rotational constant of the higher energy band is substantially smaller. It is thus reasonable to assign the first system to the (0–0) band of the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition, and the second to the (1–0) transition terminating on the first vibrationally excited level of the  $b^{3}\Sigma^{-}$  state.

The large change in the rotational constant with vibrational excitation is dramatically evident in the spectrum itself. For the (0–0) band, in which  $B'_v > B''_v$ , the Q branch is shaded to the blue. In the first vibrationally excited state,  $B'_v < B''_v$ , and the Q branch is red shaded. The large change in internuclear distance to which we must attribute this difference in rotational constant suggests a large vibrational anharmonicity. Approximating the  $b^{3}\Sigma^{-}$  potential by a Morse function, we can estimate  $\omega_e x_e$  from  $\alpha_e$  by<sup>31</sup>

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B_e^3}}{\omega_e} - \frac{6B_e^2}{\omega_e},\tag{5}$$

in which  $\omega_e x_e$  determines  $\omega_e$  when combined with the experimental v=0 to v=1 spacing ( $\omega_e = \omega_{10} + 2\omega_e x_e$ ). We solve Eq. (5) to obtain  $\omega_e x_e = 275 \text{ cm}^{-1}$ , confirming that the doubly excited  $b^{3}\Sigma^{-}$  state is substantially more anharmonic than the  $X^{1}\Sigma^{+}$  state or the Rydberg states (and by implication the AlH<sup>+</sup> cation). This value of the anharmonicity yields  $\omega_e = 2464 \text{ cm}^{-1}$ , which differs sharply with estimates based on the early emission data, but fits with the trend predicted for this valence doubly excited state by CI calculations using pseudopotential techniques to simulate core correlation effects.<sup>20</sup>

Note, however, that this large anharmonicity is much greater than that typical for hydrides with reasonable Morse potentials.<sup>22</sup> This suggests that the  $b^{3}\Sigma^{-}$  potential is highly distorted, perhaps by an avoided crossing that might be a factor in this state's large variation in spin-orbit coupling with vibrational quantum number. Such distortion implies that the usual power-series expansion for vibrational energy levels will not converge after having included terms to only second order in the vibrational quantum number. Thus, extrapolation to higher vibrational levels may not be accurate. Keeping this provision in mind, Table VIII summarizes the equilibrium rovibrational parameters derived for  $b^{3}\Sigma^{-}$  from the spectroscopic data.

# 3. Intensities and spin–orbit coupling in the b $^3\Sigma^-$ state

One might regard  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition as doubly forbidden in the sense that it violates two selection rules,  $\Delta S = 0$  and  $\Sigma^+ \leftarrow / \rightarrow \Sigma^-$ . However, only one first-order perturbation is required to lend intensity to this transition by spin-orbit coupling. Facilitating,  $\Delta \Omega = 0$  upper state interactions can mix e parity  ${}^{3}\Sigma^{-}$   $F_{1}$  and  $F_{3}$  components with nearby  ${}^{1}\Sigma^{+}$  and  ${}^{1}\Pi_{e}$  states, and the f parity  ${}^{3}\Sigma^{-}F_{2}$ components with  ${}^{1}\Pi_{f}$  levels. In the ground state, transition intensity to  $b^{3}\Sigma^{-}$  can be induced by interactions mixing  $X^{1}\Sigma^{+}$  with  ${}^{3}\Sigma_{0}^{-}$  and  ${}^{3}\Pi_{0e}$ . The ground state of AlH is electronically well isolated, so that states with the potential to perturb  $X^{1}\Sigma^{+}$  would appear to be all relatively distant, and we look first to the manifold of upper states for the source of transition intensity in the present case. In the neighborhood of the  $b^{3}\Sigma^{-}$  state we know from our own experiment that there exists at least one  ${}^{1}\Sigma^{+}$  state, which we have assigned to be  $C^{1}\Sigma^{+}$ . Coupling with this state would lend one-electron character to this excitation, and account for the branch intensity patterns discussed above by promoting a parallel (0-0) transition.

We have no information about excited  ${}^{1}\Pi$  states, but we do see strong experimental intensity in the  $(1-0) {}^{Q}Q$ branch and no discernible transitions to  ${}^{Q}P + {}^{Q}R$ . This means that there must be a perpendicular component to the transition moment for this band comparable in magnitude to its  $\mu_{\parallel}$ , which suggests that a  ${}^{1}\Pi$  state exists nearby and crosses the diabatic potential of  $b {}^{3}\Sigma^{-}$  very near v=1. The large anharmonicity of the  $b {}^{3}\Sigma^{-}$  potential may account for the strong variation in coupling with vibrational quantum number.

Therefore, if upper-state perturbations are the sole

cause of  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition intensity, then, on the basis of observed linestrengths, we can suggest provisionally that spin-orbit mixing in the v=0 level of  $b^{3}\Sigma^{-}$  is confined largely to a  ${}^{1}\Sigma^{+}$  state, perhaps  $C^{1}\Sigma^{+}$ , while  $b^{3}\Sigma^{-}v=1$  couples to a comparable degree with facilitating  ${}^{1}\Sigma^{+}$  and  ${}^{1}\Pi$  states, giving rise to a  $\mu_{1}:\mu_{\parallel}$  ratio for the (1-0) transition of nearly one. A higher resolution spectrum of the (0-0) Q branch, separating its components, is needed to confirm our picture of the v=0 state.

The other possible source of intensity in the AIH  $b^{3}\Sigma^{-}$  spectrum is via perturbation of the ground state by the triplet counterpart of the first excited  $A^{1}\Pi$  state,  $a^{3}\Pi$ . Emission results<sup>13,14</sup> place the  $T_{0}$  of the *b*-*a* transition at 26 217 cm<sup>-1</sup>. From this information together with our frequency for the  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$  transition, we can estimate the absolute position of the  $a^{3}\Pi$  state. We obtain 15 557.4 cm<sup>-1</sup>. This distance from  $X^{1}\Sigma^{+}$ , which, interestingly, is bracketed by available theoretical estimates,<sup>19,20</sup> seems too great to contribute significant perpendicular intensity to  $b^{3}\Sigma^{-}-X^{1}\Sigma^{+}$ . Furthermore, ground-state perturbations cannot explain the large difference in spin-orbit coupling strength clearly evident in the spectrum of  $b^{3}\Sigma^{-} v = 1$  compared with v=0.

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