

## Emission spectra of TiH and TiD near 938 nm

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High resolution, near infrared emission spectra of TiH and TiD have been recorded with a Fourier transform spectrometer. The TiH and TiD molecules were made in a titanium hollow cathode lamp operated with a mixture of neon and hydrogen or deuterium gases. A heavily perturbed band system near 938 nm is assigned as a  ${}^4\Phi-X{}^4\Phi$  electronic transition. Line positions and approximate spectroscopic constants are reported for the 0–0 band of the new transition. The  ${}^4\Phi-X{}^4\Phi$  TiH transition might potentially be observed in late M-type stars and in L-type brown dwarfs. © 2003 American Institute of Physics. [DOI: 10.1063/1.1539848]

### INTRODUCTION

There has been a revival of interest in the spectroscopy of transition metal hydrides in part because they are prominent in the spectra of “brown dwarfs”,<sup>1,2</sup> faint substellar objects that have properties that lie between the coolest oxygen-rich stars (M-type) and giant planets such as Jupiter. L-type brown dwarfs have surface temperatures of about 1300–2000 K and have prominent absorption bands of FeH and CrH near  $1\ \mu\text{m}$ .<sup>2</sup> The metal hydrides VH and TiH are also candidates for detection in brown dwarfs and we report here on a new near infrared TiH band system.

The spectrum of TiH was first observed in shock tube studies by Smith and Gaydon<sup>3</sup> and tentatively analyzed near 530 nm by Gaydon.<sup>4</sup> Yerle used their results in a comparison with the spectra of  $\alpha$  Ori,  $\alpha$  Sco, and  $\delta$  Vir for the first tentative stellar identifications.<sup>5</sup> Steimle *et al.*<sup>6</sup> measured the same 535 nm band by laser excitation spectroscopy and assigned the  ${}^4\Gamma_{5/2}-X{}^4\Phi_{3/2}$  subband. Lindgren<sup>7</sup> later reported two laboratory recordings of TiH bands at 530 and 939 nm. The visible band was analyzed by Launila and Lindgren<sup>8</sup> as a  ${}^4\Gamma-X{}^4\Phi$  transition. The near-infrared band was also recorded by Bernath and Ram<sup>9</sup> and these data constitute the basis for this paper.

Some additional experimental data are available for TiH. Chertihin and Andrews<sup>10</sup> measured the infrared absorption spectra of TiH and TiD isolated in an argon matrix at 10 K. The fundamental vibrational bands were found at  $1385.3\ \text{cm}^{-1}$  for TiH and  $1003.6\ \text{cm}^{-1}$  for TiD. Based on the reac-

tion thresholds of  $\text{Ti}^+$ , Chen *et al.*<sup>11</sup> derived the dissociation energy ( $D^0$ ) of TiH as  $2.12(9)\ \text{eV}$  ( $48.9\pm 2.1\ \text{kcal mol}^{-1}$ ;  $205\pm 9\ \text{kJ mol}^{-1}$ ). On the theoretical front, numerous *ab initio* calculations of the properties of TiH have been carried out. The early work established the ground state as  $X{}^4\Phi$  and discussed the formation of the metal-hydride bond.<sup>12–14</sup> The most extensive calculation of the properties of numerous states of TiH is by Anglada *et al.*,<sup>15</sup> who predict that there are a number of electronic transitions in the  $1\ \mu\text{m}$  region, of which a  ${}^4\Phi-X{}^4\Phi$  transition should be the most intense. More recent theoretical efforts have focused on improving the basis set for Ti,<sup>16</sup> on the application of density functional methods,<sup>17</sup> and on the inclusion of relativistic effects such as spin–orbit coupling.<sup>18</sup>

### EXPERIMENTAL PROCEDURE

The 938 nm band system of TiD appeared to be less perturbed than the corresponding TiH transition and more amenable to analysis. Unfortunately no TiD ground state combination differences were available to assist in making the assignments. For TiH, a complete analysis of all four subbands of the 0–0 vibrational band of the  $530\ \text{nm}\ {}^4\Gamma-{}^4\Phi$  system was carried out by Launila and Lindgren.<sup>8</sup> Therefore as a first step, the corresponding 530 nm band of TiD was studied.<sup>19</sup> This spectrum was recorded in Stockholm in the same way as the corresponding hydride band.<sup>8</sup>

The near infrared emission spectra of TiH and TiD were

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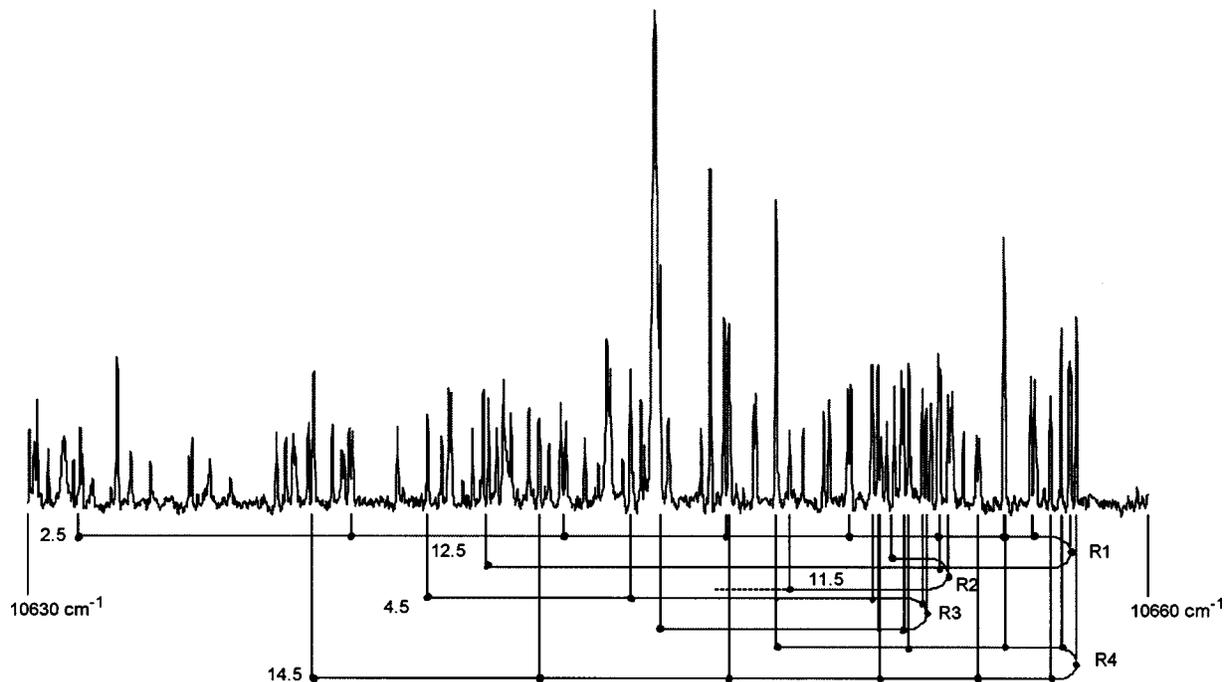


FIG. 1. A portion of the  ${}^4\Phi-X^4\Phi$  TiH spectrum in the region of the  $R$  heads. The strong feature at  $10\,646.6\text{ cm}^{-1}$  is an atomic line. Many lines from an overlapping TiH system are also present.

observed with a titanium hollow cathode lamp prepared by inserting a solid titanium rod in the hole in a copper block. The central part of the rod was bored through to provide about a 1-mm-thick layer of Ti metal on the inside of the hollow cathode. The TiH and TiD molecules were formed in separate experiments. For TiH the lamp was operated at a current of 360 V, 425 mA with a slow and steady flow of about 2 Torr of Ne and 100 mTorr of  $\text{H}_2$ . The spectra were recorded with the 1 m Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. The spectrometer was equipped with an UV beam splitter and silicon photodiode detectors. The spectrum in the  $9600\text{--}18\,000\text{ cm}^{-1}$  region was recorded using the UV beam splitter and an OG570 filter by coadding 10 scans in 66 min of integration at  $0.02\text{ cm}^{-1}$  resolution. The TiD molecules were made under similar conditions by discharging a mixture of about 2 Torr of Ne and 70 mTorr of  $\text{D}_2$ , and the spectrum of TiD was recorded by coadding 6 scans at  $0.02\text{ cm}^{-1}$  resolution in 40 min of integration.

The line positions were extracted from the observed spectra by using a data reduction program called PC-DECOMP developed by Brault at Kitt Peak. The peak positions were determined by fitting a Voigt line shape function to each spectral feature. In addition to the TiH and TiD bands, the spectra contained numerous Ti and Ne atomic lines. The molecular lines were calibrated using the Ne line positions of Palmer and Engleman.<sup>20</sup> The precision of measurements of strong and unblended lines of this transition is expected to be of the order of  $\pm 0.003\text{ cm}^{-1}$ .

## ANALYSIS AND TREATMENT OF DATA

The TiH and TiD 938 nm spectra show some of the same traits which have made the analysis of other transition metal hydride systems challenging: they are many-line spectra, with branches of widely and irregularly spaced lines. In the present instance, the TiD spectrum looked superficially somewhat better behaved than its TiH counterpart, although both spectra suffer extensively from perturbations. The most immediate evidence of perturbation may be noted from the observation that many, but not all lines, consist of resolved  $\Lambda$ -doublets with a splitting which varies with  $J$  erratically (*vide infra*).

Our analysis began with the TiD spectrum. It exhibits four subbands, each with a short, weak  $Q$  branch, flanked by  $P$  and  $R$  branches. Unfortunately the  $R$ -branch heads in all four subbands lie close together giving rise to a highly congested and initially confusing region between  $10\,640$  and  $10\,660\text{ cm}^{-1}$  (Fig. 1). The observed  $P$ ,  $Q$ , and  $R$  structure is characteristic of a  $\Delta\Lambda=0$  transition, and a comparison of rotational second combination differences confirmed that the lower state is the molecular ground state,  $X^4\Phi$ . The electronic transition responsible for the 938 nm titanium hydride spectrum is thus identified as  ${}^4\Phi-X^4\Phi$  in very satisfactory agreement with theoretical predictions.<sup>15</sup> No measurable  $\Lambda$ -doubling is evident in line features belonging to either the  ${}^4\Phi_{9/2}-{}^4\Phi_{9/2}$  or  ${}^4\Phi_{7/2}-{}^4\Phi_{7/2}$  subbands in the TiD spectrum, where observations range to  $J'=25.5$  and  $20.5$ , respectively. For the  ${}^4\Phi_{5/2}-{}^4\Phi_{5/2}$  subband a splitting occurs abruptly at  $J'=11.5$ , and for the  ${}^4\Phi_{3/2}-{}^4\Phi_{3/2}$  subband at  $J'=12.5$ . A listing of the TiD assignments is given in Table I. The TiH

TABLE I. Rotational lines ( $\text{cm}^{-1}$ ) in the  ${}^4\Phi-X{}^4\Phi$  band of TiD.

$J$	$R_1$	$Q_1$	$P_1$	$R_2$	$Q_2$	$P_2$
1.5				10 649.1801		
2.5				10 652.4863	10 635.9574	
3.5				10 655.3099	10 634.0424	10 617.5152
4.5				10 657.6097	10 631.5792	10 610.3093
5.5				10 659.3870	10 628.5905	10 602.5463
6.5				10 660.6534	10 625.0433	10 594.2289
7.5				10 661.3647		10 585.3738
8.5				10 661.6082		10 575.9794 <sup>a</sup>
9.5				10 661.3647		10 566.0422
10.5				10 660.7264/0.6534		10 555.6076
11.5	10 661.7806			10 659.9889/9.7002		10 544.6902
12.5	10 660.9944		10 538.6622			10 533.3888/3276
13.5	10 659.7713/9.1566		10 529.3154			10 521.9953/7086
14.5	10 656.0428/5.9238 <sup>a</sup>		10 518.2233/8.1251			
15.5	10 653.4010		10 506.6929/6.5184			
16.5	10 650.0381		10 492.6564/2.5184			
17.5	10 645.0255/4.7330		10 479.7245			
18.5	10 641.1515/1.0943		10 466.0833			
19.5			10 450.8354/0.5439			
20.5			10 436.7456/6.6008			
	$R_3$	$Q_3$	$P_3$	$R_4$	$Q_4$	$P_4$
3.5	10 649.2782	10 626.7453				
4.5	10 651.6964	10 624.1384	10 601.6250	10 645.4659		
5.5	10 653.5716	10 620.9728	10 593.4118	10 647.8318	10 611.9236	
6.5	10 654.9276	10 617.2532	10 584.6430	10 649.5676	10 608.3601	10 572.4544
7.5	10 655.7043	10 612.9920	10 575.3265	10 650.6726	10 604.2232	10 563.0107
8.5	10 655.9238	10 608.1926	10 565.4797	10 651.1418	10 599.5066	10 553.0590
9.5	10 655.6032	10 602.8485	10 555.1094	10 650.9868	10 594.2289	10 542.5906
10.5	10 654.7091		10 544.2069	10 650.2072	10 588.3712	10 531.6038
11.5	10 653.2466		10 532.7945	10 648.8071	10 581.9424	10 520.0963
12.5	10 651.2207		10 520.8693	10 646.7912		10 508.0692
13.5	10 648.6263		10 508.4355	10 644.1737		10 495.5041
14.5	10 645.4659		10 495.5041	10 640.9426		10 482.4530
15.5	10 641.7408		10 482.0448	10 637.1147		10 468.8636
16.5	10 637.4406		10 468.0953	10 632.6889		10 454.7415
17.5			10 453.6478	10 627.6576		10 440.1484
18.5	10 627.1922		10 438.75 <sup>a</sup>	10 622.0394		10 425.0244
19.5				10 615.8268		10 409.3857
20.5			10 407.3726	10 609.0292		10 393.2440
21.5			10 391.0280	10 601.6332		10 376.5970
22.5				10 593.6679		10 359.4502
23.5				10 585.1086		10 341.8029
24.5				10 575.9794		10 323.6629
25.5						10 305.0319

<sup>a</sup>Badly blended line.

spectrum is qualitatively similar but there essentially all of the observed lines in the  ${}^4\Phi_{5/2}-{}^4\Phi_{5/2}$  and  ${}^4\Phi_{3/2}-{}^4\Phi_{3/2}$  subbands show resolved doubling. Table II gives the TiH assignments.

Previous studies of the spectra of TiH and TiD in the

visible region have established that in both cases the ground state is unperturbed.<sup>8,19</sup> The line splittings observed in the 938 nm spectra come exclusively from splittings in the upper  ${}^4\Phi$  state: i.e.,  $R(J-1)$  and  $P(J+1)$  have the same splitting. The experimental data confirm this and are summarized in

TABLE II. Rotational lines ( $\text{cm}^{-1}$ ) in the  ${}^4\Phi-X{}^4\Phi$  band of TiH ( $\Lambda$  components).

$J$	$R_1$		$Q_1$		$P_1$	
2.5	10 631.4847	10 631.2306				
3.5	10 638.7108	10 638.6233				
4.5	10 644.4282	10 644.2823	10 598.1652 <sup>b</sup>	10 598.0009	10 559.4615	10 559.2139
5.5	10 648.7770	10 648.6496	10 594.4217	10 594.2816	10 548.0817	10 547.9981
6.5	10 652.0624	10 651.9802	10 589.2314	10 589.1191	10 534.8865	10 534.7406
7.5	10 654.4453	10 654.3968	10 582.8277	10 582.7506	10 520.0090	10 519.8896
8.5	10 656.1407	10 656.1407			10 503.7971	10 503.7134
9.5	10 656.9646	10 656.8553			10 486.4582	10 486.4057
10.5	10 657.9385	10 657.8976			10 468.2534	10 468.2534
11.5	10 654.4453				10 449.0793	10 448.9727
12.5	10 642.3547	10 642.2157			10 429.9909	10 429.9529
13.5						
14.5					10 374.2841	10 374.1474
	$R_2$		$Q_2$		$P_2$	
8.5	10 653.2219	10 653.0298				
9.5	10 654.6871	10 654.6210				
10.5	10 650.4207				10 452.0224	10 451.8276
11.5	10 649.4548	10 648.0410			10 432.3291	10 432.2630
12.5					10 407.1640	
13.5					10 385.5000	10 384.0890
	$R_3$		$Q_3$		$P_3$	
4.5	10 640.7340					
5.5	10 646.1397		10 582.0540			
6.5	10 650.0481		10 575.4123		10 511.3442	
7.5	10 652.6376		10 567.8004		10 493.1800	
8.5	10 653.9758		10 559.2139		10 474.3943	
9.5	10 654.0796		10 549.64 <sup>b</sup>		10 454.8843	
10.5	10 653.4782				10 434.5561	
11.5	10 652.7860				10 413.4537	
12.5	10 646.9325				10 391.6750	
13.5					10 370.1911	
14.5					10 343.7786	
	$R_4$		$Q_4$		$P_4$	
4.5	10 650.0481					
5.5	10 653.6121		10 576.4813			
6.5	10 656.1824		10 569.6617		10 492.5312	
7.5	10 657.6786		10 561.7148		10 475.1951	
8.5	10 658.0784		10 552.6870		10 456.7259	
9.5	10 657.3888		10 542.6131		10 437.2244	
10.5	10 655.4952	10 655.4184	10 531.5030		10 416.7356	
11.5	10 652.8765	10 652.7860			10 395.3032	
12.5	10 648.8215	10 648.7770			10 372.90 <sup>a</sup>	
13.5	10 643.7063				10 349.8131	10 349.7259
14.5	10 637.6684	10 637.5312			10 325.5508	10 325.5089
15.5					10 300.40 <sup>a</sup>	
16.5					10 274.6013	10 274.4600

<sup>a</sup>Measurement approximate; overlapped by strong Ti atomic line.<sup>b</sup>Badly blended line.

Table III. Such doubling of the  ${}^4\Phi$  state comes from interaction with a neighboring  $\Sigma$  state but requires participation of intermediary  $\Pi$  and  $\Delta$  states. Rotational levels in a diatomic hydride are widely spaced and it is not surprising to find that the complex interactions involved result in splittings, which vary irregularly with  $J$ . We have no specific knowledge of the locations of possible perturbing levels or of the strengths of the interactions. For this reason we have neglected the  $\Lambda$  doubling in our treatment of the rotational data and have used average positions.

Since the ground states had previously been characterized the line assignments from the present analysis were used to obtain upper state term values, which were fitted to a  ${}^4\Phi$  Hamiltonian:

$$\mathbf{H} = T_i + B\mathbf{N}^2 - D\mathbf{N}^4 + H\mathbf{N}^6 + (\gamma + \gamma_D\mathbf{N}^2)\mathbf{N}\cdot\mathbf{S},$$

where  $\mathbf{N} = \mathbf{J} - \mathbf{S}$  and  $i = 1, 2, 3, \text{ or } 4$ .

TABLE III.  $\Lambda$  doubling ( $\text{cm}^{-1}$ ) in the spectra of TiH and TiD.

TiH	${}^4\Phi_{3/2}-{}^4\Phi_{3/2}$			${}^4\Phi_{5/2}-{}^4\Phi_{5/2}$		${}^4\Phi_{9/2}-{}^4\Phi_{9/2}$	
	$R(J)$	$P(J)$	$Q(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
3.5	0.2541	0.2476					
4.5	0.0875	0.0836					
5.5	0.1459	0.1459	0.1401				
6.5	0.1274	0.1194	0.1123				
7.5	0.0822	0.0837	0.0771				
8.5	0.0485	0.0525					
9.5	0.0	0.0					
10.5	0.1093	0.1066		0.1921	0.1948		
11.5	0.0409	0.0380		0.0661	0.0661	0.0768	a
12.5	0.0	0.0		0.0	0.0	0.0905	0.0872
13.5	0.1390	0.1367		1.4138	1.4110	0.0445	0.0419
14.5						0.0	a
15.5						0.1372	0.1413
TiD							
11.5				0.0730	0.0612		
12.5				0.2887	0.2887		
13.5	0.0871	0.0982					
14.5	0.6137	0.6123					
15.5	0.1190 <sup>b</sup>	0.1380					
16.5	0.0	0.0					
17.5	0.0	0.0					
18.5	0.2925	0.2915					
19.5	0.3947						

<sup>a</sup>Line obscured by Ti atomic line.

<sup>b</sup>Line badly overlapped.

RESULTS AND DISCUSSION

Data from previous and the present experiments were combined to obtain improved molecular constants for the ground state. The TiH and TiD fits using the above-mentioned Hamiltonian yielded the molecular constants listed in Table IV. Attempts to fit the upper state term values to a similar model were less rewarding. Figure 2 shows a

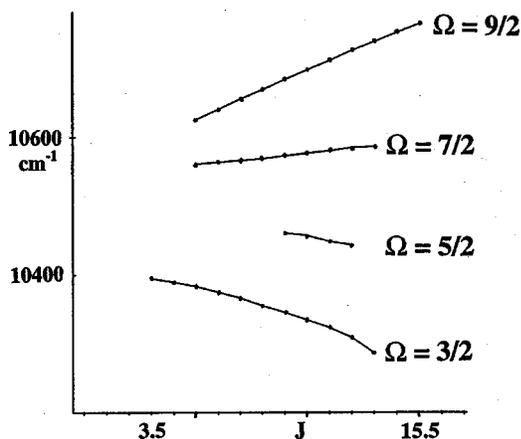


FIG. 2. A reduced term value plot for the excited  ${}^4\Phi(v=0)$  level of TiH. A quantity  $4.825J(J+1) - 1.3 \times 10^{-4}[J(J+1)]^2$  has been subtracted from the term values.

TABLE IV. Molecular constants ( $\text{cm}^{-1}$ ) for the ground state of titanium hydride. The numbers in parentheses represent standard deviations for the parameters in units of the last quoted decimal place.

	TiH	TiD
$A_0$	33.20(7)	33.42(5)
$B_0$	5.3564(4)	2.754 88(8)
$10^4 D_0$	2.56(2)	0.692(3)
$10^9 H_0$	...	1.4(2)
$10^2 \gamma_0$	19.0(9)	7.4(4)
$r_0$ (nm)	0.1779	0.1773
rms	0.0259	0.0067

plot of the TiH upper state term values. Large and numerous perturbations are present and this behavior is reflected in the quality of the fits obtained. For TiD the perturbations are concentrated in the  $F_1$  and  $F_2$  components. The results from the fit to upper state term values are given in Table V.

There is quite striking agreement between the energy predicted theoretically for the  $1\delta 3\pi 6\sigma 7\sigma^2\{{}^4\Phi\} \leftarrow 1\delta 3\pi 7\sigma^2 8\sigma\{X{}^4\Phi\}$  transition and the experimental findings reported here. The  $8\sigma$  orbital is a mix of  $4s-4p$  on Ti and  $1s$  on H and is essentially nonbonding. The  $6\sigma$  orbital has predominantly Ti  $3d\sigma$  character. Several recent estimates of the ground state TiH equilibrium bond length,  $r_e$  (nm), have been made using various approximations: 0.1744–0.1798;<sup>17</sup> 0.1836;<sup>15</sup> 0.1852–0.1873,<sup>18</sup> which can be compared with our experimental  $r_0$  value of 0.1779 nm. The excited  ${}^4\Phi$  state geometry has been calculated only by Anglada *et al.*<sup>15</sup> They predict a 0.042 nm increase in bond length upon  $8\sigma \rightarrow 6\sigma$  electron promotion and this is in modest agreement with the 0.088 nm increase we observe.

On the short wavelength side of the  ${}^4\Phi-X{}^4\Phi$  transition there are a number of branches between 938 and 910 nm. These branches were initially confusing until it was realized that they do not belong to the  ${}^4\Phi-X{}^4\Phi$  transition. Further study will be necessary before the nature of these additional

TABLE V. Molecular constants ( $\text{cm}^{-1}$ ) obtained for the excited  ${}^4\Phi$  State in TiH and TiD. The numbers in parentheses represent standard deviations for the parameters in units of the last quoted decimal place.

	TiH	TiD
$T_1$	10 453.0(4)	10 465.7(3)
$T_2$	10 559(1)	10 562.2(2)
$T_3$	10 642.5(7)	10 653.8(3)
$T_4$	10 723.3(5)	10 742.3(3)
$B_0$	4.859(5)	2.485(2)
$10^4 D_0$	2.7(2)	0.66(2)
$10^2 \gamma_0$	-22(2)	-7(1)
$r_0$ (nm)	0.1867	0.1867
No. of term values	29	61
rms	0.42	0.43

spectral features can be classified. One possibility is that the  $^4\Sigma^- - ^4\Sigma^-$  transition, predicted by Anglada *et al.*<sup>15</sup> to have relatively high intensity near  $11\,000\text{ cm}^{-1}$ , is responsible. It also arises from an  $8\sigma \rightarrow 6\sigma$  electron excitation.

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