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Fourier transform emission spectroscopy of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2

by S. A. ROGERS†, C. R. BRAZIER and P. F. BERNATH‡
Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.
and J. W. BRAULT
National Solar Observatory, National Optical Astronomy Observatories, Tucson, Arizona 85726, U.S.A.

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The 0–0 and 1–1 bands of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2 were observed near 4700 cm^{-1}. The He_2 molecule was detected in emission from a hollow cathode discharge through 4 torr of He gas with a high-resolution Fourier transform spectrometer. A complete set of fine structure constants, including Λ-doubling parameters for the $b\,^3\Pi_g$ state, were determined.

1. Introduction

The He_2 molecule was the first Rydberg molecule to be discovered [1, 2]. Since 1913 many measurements have been made on He_2 and other rare gas dimers (e.g. [3–7]). The additional Rydberg molecules RgH (Rg = He [8], Ne [9], Ar [10], Kr [11] and Xe [12]), H_3 [13, 14] and NH_4 [15] have also been discovered.

Among the more recent investigations of the He_2 spectra are the papers of D. Ginter, M. Ginter and co-workers [16–21]. Several groups have observed absorption or laser excitation spectra from the metastable $a\,^3\Sigma_u^+$ state of He_2 [5, 22–28]. The fine structure of $v = 0$ of the $a\,^3\Sigma_u^+$ is known very accurately from radio frequency measurements in a molecular beam [29–31]. The optogalvanic spectrum of the $f\,^3\Delta_u$–$b\,^3\Pi_g$ transition has also been detected [32].

Gellene and Porter studied the rare gas dimers He_2, Ne_2 and Ar_2 by the neutralized ion beam method [33]. There have also been many theoretical calculations [34–38] of the excited state potential curves of He_2, including some which combine scattering data [39] with *ab initio* theory [40–42].

In the infrared region, Herzberg and Jungen [43] have analysed the 4*f*–3*d* Rydberg complex of He_2 while Solka *et al.* [44] observed the $B\,^1\Pi_g$–$A\,^1\Sigma_u^+$ transition. The $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition near 4800 cm^{-1} was detected by Hepner and Herman in 1956 [45] and by Gloersen and Dieke in 1965 [46]. We report here new observations of the 0–0 and 1–1 bands of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2. These Doppler-limited measurements, combined with the previous radio frequency measurements [29–31] provide a very precise set of molecular constants for both the $a\,^3\Sigma_u^+$ and $b\,^3\Pi_g$ states. Although the $b\,^3\Pi_g$ and $a\,^3\Sigma_u^+$ states are well known, full resolution of the triplet splittings required intermodulated optogalvanic experiments

† Present address: Department of Chemistry, University of Colorado, Boulder, Colorado 80309, U.S.A.

‡ Alfred P. Sloan Fellow.

[32] or radio frequency measurements [29–31] or, in our work, infrared observations.

2. Experimental details

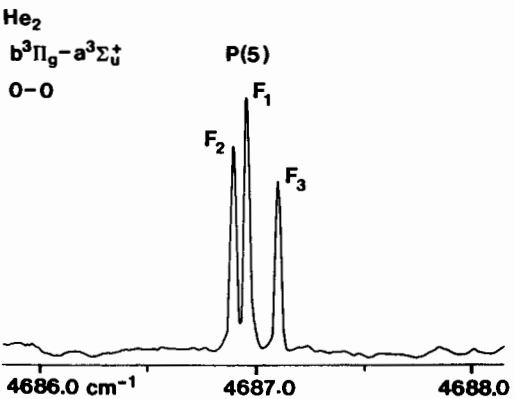
The emission spectrum of He_2 was excited in an Ni hollow cathode discharge operated at 280 mA. A flow of He gas at 4 torr pressure was maintained through the hollow cathode. The emission from the discharge was observed with the Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. The 1850–5500 cm^{-1} interval was covered by an InSb detector with a Ge filter. Ten scans were co-added in 1·3 hours of integration with an unapodized resolution of 0·01 cm^{-1}.

The spectrum was calibrated with an absolute accuracy of about $\pm 0{\cdot}002\,cm^{-1}$ by detection of emission from He atomic lines. A comparison of several He atomic lines in our spectrum with the corresponding lines in another spectrum containing both He and Ar provided the calibration of our wavenumber scale. The precision of our measurements is about $\pm 0{\cdot}001\,cm^{-1}$ for the strongest lines of the 0–0 band of He_2. This precision is consistent with the observed linewidth (0·03 cm^{-1}) and signal-to-noise ratio (≈ 25) for the strongest lines.

3. Results and discussion

The interferograms were transformed by G. Ladd to provide the spectrum. The spectrum contained He atomic lines, the $B\,^1\Pi_g$–$A\,^1\Sigma_u^+$ transition (0–0 and 1–1 bands) of He_2 [44], some of the 4*f*–3*d* Rydberg complex He_2 lines previously observed by Herzberg and Jungen [43], as well as the 0–0 and 1–1 bands of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition. The $B\,^1\Pi_g$–$A\,^1\Sigma_u^+$ line positions agree with previous observations [44] ($\pm 0{\cdot}003\,cm^{-1}$) and our Ge filter eliminates most of the 4*f*–3*d* complex of He_2. One of the strongest lines, *P*(5), of the 0–0 band of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition is displayed in the figure.

The line positions of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition were measured with a data reduction program called DECOMP, which was developed at Kitt Peak. To find the line positions, a Voigt lineshape function was fitted to the He_2 lines in a nonlinear least-squares procedure. The line positions for the 0–0 and 1–1 bands are provided in tables 1 and 2.



The $P(N = 5)$ line of the 0–0 band $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2. The F_1 (F_2, F_3) spin-component has $J'' = 6(5, 4)$.

Table 1. (*a*) Measured wavenumbers of the 0–0 band of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2 †.

N	P_1	P_2	P_3	R_1	R_2	R_3
1	—	—	—	4796·7700(12)	4796·7534(23)	4797·0112(3)
3	4720·9529(5)	4720·9386(9)	4721·2266(2)	4823·1477(−5)	4823·0839(−10)	4823·2841(−4)
5	4686·9660(3)	4686·9026(−9)	4687·1060(−2)	4847·1063(−2)	4847·0253(−6)	4847·2025(2)
7	4651·0391(1)	4650·9583(−4)	4651·1369(4)	4868·5907(5)	4868·5005(1)	4868·6658(0)
9	4613·3296(1)	4613·2394(−4)	4613·4060(1)	4887·5543(−1)	4887·4592(3)	4887·6181(1)
11	4573·9965(−10)	4573·9029(10)	4574·0622(7)	4903·9704(19)	4903·8685(−9)	4904·0241(−4)
13	4533·2121(4)	4533·1120(−3)	4533·2676(−3)	4917·8184(−1)	4917·7166(−1)	4917·8689(−5)
15	4491·1502(−1)	4491·0482(2)	4491·2006(−7)	4929·1009(−54)	4929·0059(34)	4929·1581(44)
17	4447·9998(−2)	4447·8969(12)	4448·0464(−10)	4937·8520(23)	4937·7411(−32)	4937·8926(−21)
19	4403·9563(2)	4403·8506(4)	4404·0001(−10)	4944·0806(−12)	4943·9776(25)	4944·1248(−3)
21	4359·2220(1)	4359·1153(6)	4359·2647(−5)			
23	4314·0097(11)	4313·9018(15)	4314·0499(−9)			
25	4268·5338(−14)	4268·4281(22)	4268·5743(−25)			
27	4223·0282(−11)	4222·9217(24)	4223·0698(−8)			

† The numbers in brackets correspond to obs.–calc. in units of $10^{-4}\,cm^{-1}$, computed with the constants of tables 3 and 4.

Table 1. (*b*) Measured wavenumbers of the 0–0 band of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2.

N	Q_1	Q_2	Q_3
1	4767·4957(0)	4767·9006(−1)	4767·5639(−1)
3	4764·9907(−1)	4765·3294(−5)	4765·0302(−15)
5	4760·4690(−8)	4760·7953(−1)	4760·4957(6)
7	4753·9694(−3)	4754·2903(3)	4753·9890(11)
9	4745·5341(−7)	4745·8525(4)	4745·5493(5)
11	4735·2254(58)	4735·5353(5)	4735·2254(−53)
13	4723·0945(46)	4723·4032(−4)	4723·0945(−45)
15	4709·2275(41)	4709·5350(−7)	4709·2275(−33)
17	4693·7122(34)	4694·0205(5)	4693·7122(−28)
19	4676·6491(32)	4676·9559(−2)	4676·6491(−20)
21	4658·1491(38)	4658·4526(−18)	4658·1491(−5)

Table 2 (*a*) Measured wavenumbers of the 1–1 band of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2.

N	P_1	P_2	P_3	R_1	R_2	R_3
1	—	—	—	4762·5876(−57)	4762·5876(46)	
3	4689·1801(11)	4689·1801(55)	4689·4485(7)	4788·2618(−4)	4788·1945(−32)	4788·3983(45)
5	4656·4052(−40)	4656·3437(−33)	4656·5513(23)	4811·6540(−4)	4811·5697(−10)	4811·7479(−37)
7	4621·8447(−13)	4621·7644(10)	4621·9408(−25)	4832·7171(−22)	4832·6280(22)	4832·7907(−30)
9	4585·6527(2)	4585·5604(6)	4585·7289(0)	4851·4180(23)	4851·3188(23)	4851·4759(−28)
11	4548·0006(48)	4547·8955(−16)	4548·0573(−27)	4867·7192(5)	4867·6190(31)	4867·7732(−11)
13	4509·0521(−7)	4508·9484(−19)	4509·1122(29)	4881·6214(2)	4881·5142(−17)	4881·6720(1)
15	4469·0137(22)	4468·9045(−20)	4469·0636(7)			
17	4428·0676(−24)	4427·9629(−3)	4428·1177(−1)			

Table 2. (*b*) Measured wavenumbers of the 1–1 band of $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ transition of He_2.

N	Q_1	Q_2	Q_3
1	4734·2094(47)	—	4734·2094(3)
3	4731·8784(−1)	4732·2105(−48)	4731·9190(59)
5	4727·6694(−8)	4727·9900(7)	4727·6925(15)
7	4721·6316(57)	4721·9411(33)	4721·6316(−72)
9	4713·7958(15)	4714·1044(23)	4713·7958(−61)
11	4704·2372(12)	4704·5440(30)	4704·2372(−22)
13	4693·0246(1)	4693·3264(−10)	4693·0246(1)
15	4680·2471(6)	4680·5456(−21)	4680·2471(35)
17	4665·9968(−47)	4666·2926(−86)	4665·9968(8)
19	4650·3999(−12)	4650·6993(−2)	4650·3999(67)

The $b\,^3\Pi_g$ and $a\,^3\Sigma_u^+$ states obey Hund's case (b) coupling so each rotational line is a triplet (figure). The three spin components F_1, F_2 and F_3 with $J = N + 1$, N and $N - 1$, respectively, result in the nine strong branches P_1, P_2, P_3, Q_1, Q_2, Q_3, R_1, R_2 and R_3, listed in tables 1 and 2. Nuclear spin statistics have eliminated all of the even N rotational states (+ parity) in the $a\,^3\Sigma_u^+$ state and half of the Λ-doubling components in the $b\,^3\Pi_g$ state (− parity).

The line positions of tables 1 and 2 were reduced to molecular constants through the use of the customary effective $\hat{N}^2$ hamiltonian for $^3\Sigma$ and $^3\Pi$ states [47]. Explicit matrix elements are provided in our paper on the $A\,^3\Pi$–$X\,^3\Sigma^-$ transition of NH [48]. Note that table VIII of the NH paper contains the matrix elements for a $^3\Sigma^-$ state. The matrix elements for a $^3\Sigma^+$ state are identical except that e is replaced by f, and f is replaced by e. Thus for $^3\Sigma^+(^3\Sigma^-)$, the F_2 levels have $e(f)$ symmetry while F_1 and F_3 have $f(e)$ symmetry.

For the 0–0 band the lines of table 1 were combined with the fine structure intervals for $N = 1$, 3 and 5 for $v = 0$ of the $a\,^3\Sigma_u^+$ state obtained by radio frequency spectroscopy of a molecular beam of He_2 [29–31] in a simultaneous nonlinear least-squares fit. The fine structure intervals for $v = 1$ of the $a\,^3\Sigma_u^+$ state are not available so only the infrared lines of table 2 were fitted. The resulting molecular constants for $v = 0$ and 1 of the $a\,^3\Sigma_u^+$ state are provided in table 3 while the $b\,^3\Pi_g$ constants are in table 4. It was not possible to simultaneously determine A_D and γ in the $b\,^3\Pi_g$ state so A_D was constrained to zero in the final fit.

The molecular constants of tables 3 and 4 are in reasonable agreement with previous determinations if differences in the hamiltonians are taken into account. For the $b\,^3\Pi_g$ state, Kawakita *et al.* [32] find $A_\pi = -0{\cdot}225\,\mathrm{cm}^{-1}$, $\lambda_\zeta(= 2\lambda) = 0{\cdot}102\,\mathrm{cm}^{-1}$, $\lambda_{\perp\perp}(= -o/2) = -0{\cdot}149\,\mathrm{cm}^{-1}$ and $\gamma = -0{\cdot}0003\,\mathrm{cm}^{-1}$, compared to $A = -0{\cdot}227$, $\lambda = 0{\cdot}0554$, $o = 0{\cdot}290$ and $\gamma = -0{\cdot}0002\,\mathrm{cm}^{-1}$ (table 4). The λ and γ parameters of the $a\,^3\Sigma_u^+$ state are essentially the same as the very precise previous determinations [29–31] since the radio frequency data were included in our fit. For the $b\,^3\Pi_g$ state we were able to determine a complete set of Λ-doubling parameters (table 4).

The effective hamiltonian parameters of tables 3 and 4 can be interpreted in terms of the electronic properties of He_2. An *ab initio* quantum chemical calculation for the $a^3\Sigma_u^+$ state [49] predicts a first order spin–spin constant of $-0{\cdot}04089\,\mathrm{cm}^{-1}$, in reasonable agreement with the observed value of $-0{\cdot}03666$ (table 3). This calculation suggests that second order spin–orbit contributions to λ, which dominate for most molecules with $^3\Sigma$ states, are small for He_2.

Table 3. Spectroscopic constants (in cm^{-1}) for the $a\,^3\Sigma_u^+$ state of He_2 †.

Constant	$v = 0$	$v = 1$
B_v	7·589199(26)	7·34875(10)
$10^4 \times D_v$	5·6228(28)	5·6557(79)
$10^8 \times H_v$	3·47(10)	2·88(18)
$10^{12} \times L_v$	−6·1(11)	—
$10^2 \times \lambda_v$	−3·6664333(84)	−6·64(27)
$10^6 \times \lambda_{Dv}$	6·5852(46)	—
$10^5 \times \gamma_v$	−8·0751(38)	—
$10^8 \times \gamma_{Dv}$	2·02(15)	—

† The numbers in parentheses refer to one standard deviation in the last digits.

Table 4. Spectroscopic constants (in cm^{-1}) for the $b\,^3\Pi_g$ state of He_2 †.

Constant	$v = 0$	$v = 1$
T_{vv}	4768·14536(20)	4734·82379(107)
B_v	7·323494(28)	7·100566(101)
$10^4 \times D_v$	5·2618(32)	5·2592(80)
$10^8 \times H_v$	3·27(12)	2·720(19)
$10^{12} \times L_v$	−5·9(14)	—
A_v	−0·22694(43)	−0·2217(26)
$10^2 \times \lambda_v$	5·545(23)	1·94(30)
$10^4 \times \gamma_v$	−2·20(18)	—
$10^4 \times p_v$	4·04(33)	7·74(88)
$10^2 \times q_v$	−2·54016(77)	−2·4705(22)
$10^6 \times q_{Dv}$	5·296(71)	4·84(12)
$10^{10} \times q_{Hv}$	−7·8(14)	—
o_v	0·29042(25)	0·2886(10)

† The numbers in parentheses refer to one standard deviation in the last digits.

For the $b\,^3\Pi_g$ state, the Λ-doubling is caused primarily by interaction with the nearest $^3\Sigma_g^+$ state ('unique perturber' interaction [50]). The $c\,^3\Sigma_g^+$ $(3p\sigma)$ state lies about $6120\,cm^{-1}$ above the $b\,^3\Pi_g(2p\pi)$. As suggested by Ginter [18], this pair of states is an example of 'accidental pure precession' [51]. In the case of normal pure precession, there are $l + 1$ diatomic electronic states which arise from a given set of degenerate nl atomic orbitals. The b and c states of He_2 cannot have a normal pure precession relationship because they correlate to different principal atomic quantum numbers in the united atom limit. However, the b and c states (like the $B\,^1\Pi_g$ and $C\,^1\Sigma_g^+$ states) have nearly the same effective principal quantum number, $n^* = n - \delta \approx 2$, because they are separated by only $6120\,cm^{-1}$ [18].

The pure precession expressions for the Λ-doubling parameters of a $^3\Pi$ state interacting with a $^3\Sigma^+$ state are [47, 52]:

$$q = \frac{4B^2}{E_\Pi - E_\Sigma} = -0{\cdot}035\,cm^{-1},$$

$$p = \frac{4AB}{E_\Pi - E_\Sigma} = 0{\cdot}0011\,cm^{-1},$$

and

$$o^{(2)} = \frac{A^2}{E_\Pi - E_\Sigma} = -8{\cdot}4 \times 10^{-6}\,cm^{-1},$$

where $l = 1$ is assumed. There is reasonable agreement with the values in table 4 for $q\,(= -0{\cdot}025\,cm^{-1})$ and $p\,(= 0{\cdot}0004\,cm^{-1})$. The experimental value of $o = o^{(1)} + o^{(2)}$ [47] is found to be much larger $(0{\cdot}29\,cm^{-1})$ than p or q. Of the components of o, the second order spin–spin contribution, $o^{(2)}$ is negligible in comparison with the first order spin–spin contribution, $o^{(1)}$. Since $o^{(2)} = -4\lambda^{(2)}$ [52] and $\lambda = \lambda^{(1)} + \lambda^{(2)}$ [47] $= 0{\cdot}055\,cm^{-1}$, the second order spin–orbit contribution, $\lambda^{(2)}$, to the spin–spin constant is also negligible in comparison to the first order ('true') spin–spin contribution, $\lambda^{(1)}$. However, the spin–rotation relationship $p = -2\gamma^{(2)}$ [52] predicts $\gamma^{(2)} = -2{\cdot}1 \times 10^{-4}$ in excellent agreement with $\gamma = \gamma^{(1)} + \gamma^{(2)} = -2{\cdot}3 \times$

$10^{-4}\,cm^{-1}$. The second order spin–orbit contribution, $\gamma^{(2)}$, to γ is (as usual) much larger than the true spin–rotation constant, $\gamma^{(1)}$.

In a paper on the fine structure of the $c\,^3\Pi_u$ state of H_2, Fontana [53] pointed out the similarity between the $b\,^3\Pi_g$ state of He_2 and the $c\,^3\Pi_u$ state of H_2 because both states correlate to $2p\pi$ in the united atom limit for the Rydberg electron. In the united atom limit, Fontana [53] finds $\lambda_\zeta = -\lambda_{\perp\perp}$, in the notation of Mizushima [32, 54] or $\lambda = o/4$, in the notation of Brown *et al.* [47]. From table 4, $o/4$ is $0{\cdot}073\,cm^{-1}$, in reasonable agreement with $\lambda = 0{\cdot}055\,cm^{-1}$.

In conclusion, the observation of the $b\,^3\Pi_g$–$a\,^3\Sigma_u^+$ infrared emission spectrum of He_2 has resulted in a set of accurate molecular constants. The interpretation of these effective molecular constants provides some insight into the electronic structure of the He_2 Rydberg molecule.

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