The Low-Lying States of He$_2$

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The near-infrared emission spectrum of He$_2$, excited in a Be hollow cathode discharge, has been recorded at high resolution using a Fourier transform spectrometer. The $c^3\Sigma_g^+–a^3\Sigma_u^+$ (0–0, 1–1, 2–2, 1–0, and 2–1) and $C^1\Sigma_g^+–A^1\Sigma_u^+$ (0–0 and 1–1) transitions have been observed in the 9000–15 000 cm^{-1} spectral region.

A global analysis of the six lowest excited states of He$_2$ ($c^3\Sigma_g^+$, $b^3\Pi_g$, $a^3\Sigma_u^+$, $C^1\Sigma_g^+$, $B^1\Pi_g$, and $A^1\Sigma_u^+$) was carried out by combining our measurements with previously reported infrared data for the $b^3\Pi_g–a^3\Sigma_u^+$ system [S. A. Rogers *et al., Mol. Phys.* **63,** 901 (1988)] and with laser measurements for the $B^1\Pi_g–A^1\Sigma_u^+$ transition [H. Solka *et al., Mol. Phys.* **60,** 1179 (1987)]. To account for the fine structure in the $a^3\Sigma_u^+$ state, high precision r.f. measurements were included in the global fit. A consistent set of improved molecular constants was derived for the $c^3\Sigma_g^+$ ($v = 0, 1,$ and 2), $b^3\Pi_g$ ($v = 0$ and 1), $a^3\Sigma_u^+$ ($v = 0, 1,$ and 2), $C^1\Sigma_g^+$ ($v = 0$ and 1), $B^1\Pi_g$ ($v = 0$ and 1), and $A^1\Sigma_u^+$ ($v = 0$ and 1) levels. A study of the vibrational dependence of these constants was also performed, leading to the equilibrium parameters for the six electronic states. © 1998 Academic Press

I. INTRODUCTION

He$_2$ is a favorite molecule for both experimentalists and theoreticians. The ground state potential of He$_2$ is very shallow and all of the excited states are Rydberg states. He$_2$ was the first excimer (excited dimer) to be discovered and is an example of a Rydberg molecule.

More than 60 electronic states are known for He$_2$ mainly through the extensive classical grating measurements of Ginter and co-workers (*1–9*). In more recent years, the $b^3\Pi_g–a^3\Sigma_u^+$ transition (*10*) and the $4f–3d$ Rydberg transition (*11*) have been measured by infrared Fourier transform emission spectroscopy. Laser measurements have been made for the $B^1\Pi_g–A^1\Sigma_u^+$ (*12*), $c^3\Sigma_g^+–a^3\Sigma_u^+$ (*13–15*), and $f^3\Delta_u–b^3\Pi_g$ (*16*) systems in the infrared and visible region. In a unique infrared emission experiment using a 6.5-MeV proton beam to excite a dense, cold sample of He gas, Brooks *et al.* (*17*) detected highly excited vibrational levels of the $a^3\Sigma_u^+$ and $b^3\Pi_g$ states.

Highly precise radio frequency (r.f.) measurements of the He$_2$ fine structure transitions have been carried out. The older work for the metastable $a^3\Sigma_u^+$ state $v = 0$, $N = 1, 3,$ and 5 (*18–20*) used the molecular beam magnetic resonance method while the more recent measurements used the r.f. laser double resonance technique (*13–15*). Bjerre and co-workers (*13–15*) use predissociative $c^3\Sigma_g^+–a^3\Sigma_u^+$ transitions of He$_2$ in a fast neutral beam to monitor r.f. absorption. In this way r.f. mea-

surements were extended to higher rotational and vibrational levels of the $a^3\Sigma_u^+$ state.

As might be expected for a molecule with only four electrons, He$_2$ has been a frequent theoretical target (*21–25*). The very existence of a ground state van der Waals dimer has been a matter of some dispute for many years. The experimental molecular beam work of Luo *et al.* (*26*) demonstrated that ground state He$_2$ can be made in a molecular beam. He$_2$ diffraction from a transmission grating (*27*) and transmission through a set of nanoscale sieves (*28*) support this conclusion. The very weakly attractive He$_2$ potential supports one vibration–rotation level. The properties of the excited states of He$_2$ have also been calculated, most notably by Yarkony (*23*).

In the course of some Fourier transform emission measurements of a Be hollow cathode filled with He gas, we inadvertently recorded the near-infrared bands of He$_2$. At the same time, P. Rosmus was completing an *ab initio* calculation of the fine structure of the $a^3\Sigma_u^+$ state (*29*). Rosmus (*29*) pointed out to us that the previous estimate (*10*) of λ, the spin–spin constant, for $v = 1$ of the $a^3\Sigma_u^+$ state was somewhat dubious. At the same time, N. Bjerre (*30*) communicated to us some unpublished r.f. measurements of the spin splittings for $v = 1$ and $v = 2$ of the $a^3\Sigma_u^+$ state. It seemed therefore useful to combine the new Fourier transform observations with all of the r.f. data and to include the published $b^3\Pi_g–a^3\Sigma_u^+$ (*10*) and $B^1\Pi_g–A^1\Sigma_u^+$ (*11*) lines in a global analysis.

II. EXPERIMENTAL DETAILS

The near-infrared emission spectrum of He$_2$ was excited in a Be hollow cathode discharge operated at a current of 600 mA with a static sample of 30 Torr of He. The spectrum of He$_2$ was

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inadvertently recorded during a search for BeN. The first He_2 spectra were recorded at lower pressures but, as noted by previous workers, the He_2 emission increases strongly with pressure. The emission from the discharge was recorded with a Bruker IFS 120 HR Fourier transform spectrometer. The $9000-15\,000$ cm^{-1} range was isolated by using a Si photodiode detector and a RG 715 red-pass filter. A total of 100 scans was co-added in 1 h of observation at an instrumental resolution of 0.1 cm^{-1}. Higher resolution spectra were not recorded because the uncooled cathode (necessary to vaporize Be) had a temperature of perhaps 1500 K. The resulting Doppler widths of the He_2 lines were about 0.1 cm^{-1}.

Much to our surprise the spectrum contained many strong Ar atomic lines, presumably originating from an Ar impurity in the He gas. Seventeen Ar atomic lines were utilized in the calibration of the spectrum, using the very accurate line positions reported by Norlen (31). The wavenumber scale was calibrated with an estimated absolute accuracy of ± 0.002 cm^{-1}. The line positions were measured by fitting Voigt lineshape functions to the He_2 lines in a nonlinear, least-squares procedure. The precision of our measurements is estimated to about ± 0.003 cm^{-1} for the unblended lines of the $C^1\Sigma_g^+ - A^1\Sigma_u^+$ transition, consistent with the observed linewidth (FWHM ≈ 0.11 cm^{-1}) and signal-to-noise ratio (~ 35 for the strongest 0–0 lines). The signal-to-noise ratio was higher for the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ transition (up to 100 for the strongest 0–0 band lines) but the precision of these lines was estimated at only ± 0.005 cm^{-1} because of the unresolved triplet fine structure.

III. ANALYSIS

A. Observed Bands

The $c^3\Sigma_g^+ - a^3\Sigma_u^+$ and $C^1\Sigma_g^+ - A^1\Sigma_u^+$ transitions were observed as well as some lines belonging to the $d^3\Sigma_u^+ - c^3\Sigma_g^+$ (0–0, 1–1, 2–2), $f^3\Sigma_u^+ - c^3\Sigma_g^+$ (0–0, 1–1, 2–2), $f^3\Pi_u - c^3\Sigma_g^+$ (0–0, 1–1, 2–2), and $f^3\Delta_u - c^3\Sigma_g^+$ (0–0) systems. These latter transitions are not included in the current analysis. Both $\Delta v = 0$ (0–0, 1–1, and 2–2) and $\Delta v = +1$ (1–0 and 2–1) bands were observed for the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ transition, while only $\Delta v = 0$ (0–0 and 1–1) bands were found for the $C^1\Sigma_g^+ - A^1\Sigma_u^+$ transition. The assigned lines are listed in Table 1 and Table 2, for the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ and $C^1\Sigma_g^+ - A^1\Sigma_u^+$ systems, respectively. Note that since the ^{4}He nucleus has a spin of zero, alternate lines are missing. All of the even N rotational levels of the lower $a^3\Sigma_u^+$ and $A^1\Sigma_u^+$ states are eliminated, as well as the odd N levels of the upper $c^3\Sigma_g^+$ and $C^1\Sigma_g^+$ states. Compared with Ginter's previous results (1) on these systems, we were able to follow the P and R branches to higher N for the strong $\Delta v = 0$ bands, but we have a few less lines for the $\Delta v = +1$ bands. Some molecular lines are overlapped by atomic lines and are not reported in Tables 1 and 2. No triplet fine structure splittings were resolved in any of the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ lines.

B. The $a^3\Sigma_u^+$, $b^3\Pi_g$, and $c^3\Sigma_g^+$ Triplet States

Preliminary fits of the new $c^3\Sigma_g^+ - a^3\Sigma_u^+$ bands were carried out ignoring the fine structure in both states. For the final fit the

new FT measurements of the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ system were merged with the previous FTIR lines of the $b^3\Pi_g - a^3\Sigma_u^+$ (0–0 and 1–1) transition reported by Rogers *et al.* (10). Also, all of the r.f. measurements available in the literature were added to the global fit, in order to account for the fine structure of the $a^3\Sigma_u^+$ state and to refine the constants of the $b^3\Pi_g$ state. The r.f. lines in the $a^3\Sigma_u^+$ state are for $v = 0$, $N = 1, 3$ (18); $v = 0$, $N = 5$ (20); $v = 0$, $N = 7, 9, 11$ (14); $v = 0$, $N = 25, 27$, 29 (15); $v = 1$, $N = 25, 27$; $v = 2$, $N = 7, 9, 11$ (15); and $v = 2$, $N = 19$. Some of these data, listed below, have never been published and were kindly communicated to us by N. Bjerre (30):

$a^3\Sigma_u^+$, $v = 1$, $N = 25$:

$$\nu_1 = 841.777 \text{ MHz}; \quad \nu_2 = 973.401 \text{ MHz}$$

$a^3\Sigma_u^+$, $v = 1$, $N = 27$:

$$\nu_1 = 820.326 \text{ MHz}; \quad \nu_2 = 952.743 \text{ MHz}$$

$a^3\Sigma_u^+$, $v = 2$, $N = 19$:

$$\nu_1 = 836.513 \text{ MHz}; \quad \nu_2 = 957.42 \text{ MHz},$$

where ν_1 refers to the $J = N \leftrightarrow J = N + 1$ transition, and ν_2 to the $J = N \leftrightarrow J = N - 1$ transition.

In the global fit, each line was weighted according to its precision: from 0.003 to 0.06 MHz for the r.f. measurements, 0.001 cm^{-1} for strong unblended lines of the $b^3\Pi_g - a^3\Sigma_u^+$ IR system, and 0.005 cm^{-1} for strong unblended lines of the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ transition. In the course of our analysis it was necessary to reassign some first lines belonging to the $b^3\Pi_g - a^3\Sigma_u^+$ transition as satellite lines. In the $b^3\Pi_g - a^3\Sigma_u^+$ 0–0 band, the 4721.2266-cm^{-1} line was reassigned as $^OP_{23}(3)$ from $P_3(3)$, the 4797.0112-cm^{-1} line from $R_3(1)$ to $^QR_{23}(1)$, the 4767.9006-cm^{-1} line from $Q_2(1)$ to $^PQ_{12}(1)$, and the 4767.5639-cm^{-1} line from $Q_3(1)$ to $^PQ_{13}(1)$. In the $b^3\Pi_g - a^3\Sigma_u^+$ 1–1 band, the 4689.4485-cm^{-1} line was reassigned as $^OP_{23}(3)$ from $P_3(3)$, while the 4734.2094-cm^{-1} line corresponds only to $Q_1(1)$, because the $Q_3(1)$ line cannot exist. The notation used in specifying the lines is $^{\Delta N}\Delta J_{F'F''}(N'')$, where $F = 1$ for $J = N + 1$, $F = 2$ for $J = N$, and $F = 3$ for $J = N - 1$, as is customary for states with Hund's case (b) coupling.

The usual effective $\hat{N}^2$ Hamiltonian for $^3\Sigma$ and $^3\Pi$ states (32) was used to reduce the experimental data to molecular constants. Explicit matrix elements for $^3\Sigma$ and $^3\Pi$ states are provided in Ref. (33). Note that Table VIII of Ref. (33) 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. Because of the extensive amount of high-quality r.f. data, we needed to use the higher-order λ_H and λ_L constants for the $a^3\Sigma_u^+$, $v = 0$ level. The matrix elements corresponding to these parameters were calculated by matrix multiplication [e.g., $\lambda_H = -(D\lambda + \lambda D)/2$), starting from the matrix elements listed in Table VIII of Ref. (33)].

The molecular constants derived from the fit are displayed in

TABLE 1

Observed Line Positions (in cm^{-1}) for the $c^3\Sigma_g^+ - a^3\Sigma_u^+$ Transition of He$_2$

	$c^3\Sigma_g^+ - a^3\Sigma_u^+$			
	0 – 0		1 – 0	
N	R(N)	P(N)	R(N)	P(N)
1	10915.4016(2)	10874.2978(69)		12354.2879(-299)
3	10935.3370(-24)	10839.5900(46)	12409.4162(16)	*a*
5	10949.1849(-5)	10799.1578(2)	12416.6830(-87)	12273.2418(91)
7	10956.8325(-22)	10753.1168(-13)	12415.3478(31)	12220.6229(-15)
9	*a*	10701.5716(-20)	12405.2325(18)	12160.0911(76)
11	10953.1296(-14)	10644.6241(-24)	12386.1802(-106)	12091.6806(79)
13	10941.5675(3)	10582.3711(-16)	12358.0381(-58)	12015.4292(-33)
15	10923.3809(12)	10514.8981(1)	*a*	11931.3723(-25)
17	10898.4451(18)	10442.2755(18)	12273.5599(64)	11839.4821(77)
19	10866.6161(16)	10364.5528(17)	12216.6663(-26)	11739.6592(-20)
21	10827.7189(-38)	10281.7588(47)	12149.9592(3844)^b	11631.7890(-196)
23	10781.5608(13)	10193.8688(-24)		
25	10727.8565(-80)	10100.8452(12)		
27	10666.3098(17)	10002.5474(-64)		
29	10596.4762(57)	9898.8109(45)		
31	10517.8136(-26)	9789.3109(1)		

	1 – 1		2 – 1	
N	R(N)	P(N)	R(N)	P(N)
1	10661.9581(-61)	10622.6401(27)		
3	10680.1338(-51)	10588.5480(-51)		11958.2902(56)
5	10691.7464(1)	10548.2848(-25)	12049.5045(93)	11913.3615(-128)
7	10696.6608(20)	10501.9370(-15)	12044.3437(207)	11859.6751(-123)
9	10694.7407(12)	10449.5919(-3)	12029.4860(-120)	11797.2316(-248)
11	10685.8368(-6)	10391.3205(11)	12004.7737(29)	11726.0907(127)
13	10669.7821(-4)	10327.1704(-6)	11969.8442(45)	11646.1221(177)
15	10646.3787(3)	10257.1703(-24)	11924.3337(19)	11557.2227(-73)
17	10615.3943(3)	10181.3123(-27)	*a*	11459.2607(-77)
19	10576.5509(-14)	10099.5483(38)	11799.5662(298)	11351.9123(-96)
21	10529.9365(4192)^b	10011.7567(56)		11234.7343(-8)
23	10473.8778(1)	9918.2019(4483)^b		11107.0314(-26)

	2 – 2	
N	R(N)	P(N)
1	10377.8486(-6)	10340.4995(-74)
3	10393.8340(-167)	10306.9292(198)
5	10402.5646(-80)	10266.4542(24)
7	10403.8404(-14)	10219.2071(9)
9	10397.4565(-4)	10165.2160(9)
11	10383.1779(-20)	10104.4790(-81)
13	10360.7231(8)	10036.9881(11)
15	10329.7245(9)	9962.6252(36)
17	10289.6919(-270)	9881.2134(-25)
19		9792.4806(10)

Note. Observed–calculated differences are reported in parentheses in the unit of the last quoted digit.

^{a} Obscured by an atomic line.

^{b} Perturbation.

Tables 3–5 for the $a^3\Sigma_u^+$, $b^3\Pi_g$, and $c^3\Sigma_g^+$ states, respectively. The ''observed–calculated'' differences returned by the fit for our FT lines are reported in Table 1. Some remarks need to be made about the results reported in Table 1. Since the fine structure was not resolved for the reported lines, each line was included three times in the fit, corresponding to the three spin–components, F_1, F_2, and F_3. However, in Table 1, only the observed–calculated values for the F_1 lines are reported. In addition, a few lines exhibit large observed–calculated values,

leading to the conclusion that the $c^3\Sigma_g^+$ ($v = 1$, $N = 22$) rotational level is perturbed by an unknown level.

In the final fit, the λ_H and λ_L constants for the $v = 1$ and $v = 2$ vibrational levels of the $a^3\Sigma_u^+$ state (see Table 3) were fixed to the values found for the $v = 0$ level because of the smaller amount of r.f. data available for the vibrationally excited levels. The γ_v constant of the $v = 1$ $b^3\Pi_g$ level was fixed to the corresponding value for the $v = 0$ level (see Table 4). Finally, since only a very limited amount of fine structure

TABLE 2
Observed Line Positions (in cm^{-1}) for the $C^1\Sigma_g^+$–$A^1\Sigma_u^+$ Transition of He$_2$

| | $C^1\Sigma_g^+ - A^1\Sigma_u^+$ | | | |
| | 0 – 0 | | 1 – 1 | |
N	R(N)	P(N)	R(N)	P(N)
1	10971.7978(-33)	10930.1396(23)	10751.8303(50)	
3	10992.2269(-104)	10895.1697(25)	10771.0417(15)	10677.4272(-50)
5	11006.6982(1)	10854.5705(5)	10784.0840(-55)	10637.4056(-5)
7	11015.1058(0)	10808.4647(0)	10790.8902(5)	10591.6856(32)
9	11017.3925(-1)	10756.9769(1)	10791.3661(23)	10540.3805(-12)
11	11013.4990(-3)	10700.2374(6)	10785.4385(-15)	10483.6311(40)
13	11003.3750(1)	10638.3787(7)	10773.0474(6)	10421.5325(-59)
15	10986.9747(3)	10571.5340(-6)	10754.1042(-1)	10354.2256(30)
17	10964.2569(0)	10499.8375(-11)		10281.7588(-5)
19	10935.1756(-74)	10423.4209(27)		
21	10899.7110(-5)	10342.3924(-8)		
23	10857.7983(26)	10256.8775(43)		
25	10809.3775(-10)	10166.9448(-85)		
27		10072.7114(8)		

Note. Observed–calculated differences are reported in parentheses in the unit of the last quoted digit.

data is available for the $c^3\Sigma_g^+$ state (*15*), the fine structure parameters for the $v = 0, 1$, and 2 vibrational levels of this state were fixed to the corresponding values of these constants for the $a^3\Sigma_u^+$ state (see Table 5).

C. The $A^1\Sigma_u^+$, $B^1\Pi_g$, and $C^1\Sigma_g^+$ Singlet States

Our FT data for the $C^1\Sigma_g^+$–$A^1\Sigma_u^+$ transition were combined with the very accurate laser measurements by Solka *et al.* (*12*) for the $B^1\Pi_g$–$A^1\Sigma_u^+$ transition. The two sets of data were weighted according to their precision, i.e., 0.003 cm^{-1} for our $C^1\Sigma_g^+$–$A^1\Sigma_u^+$ lines and 0.002 cm^{-1} for the $B^1\Pi_g$–$A^1\Sigma_u^+$ laser measurements. Both systems include the 0–0 and 1–1 bands. Despite our efforts, we were not able to observe the 1–0 band of the $C^1\Sigma_g^+$–$A^1\Sigma_u^+$ system, so we

used Ginter's value of 1790.75 cm^{-1} (*1*) for the $v = 0$ and $v = 1$ vibrational interval in the $A^1\Sigma_u^+$ state in our fit. We used the usual simple energy level expressions for the $^1\Sigma_u^+$ and $^1\Pi_g$ states, with the q and q_D parameters to account for the Λ doubling in the $B^1\Pi_g$ state:

$$F(J) = BJ(J + 1) - D[J(J + 1)]^2$$
$$+ H[J(J + 1)]^3 + L[J(J + 1)]^4 \qquad [1]$$
$$\pm \frac{\delta_{1,\Lambda}}{2}[qJ(J + 1) + q_D[J(J + 1)]^2]$$

TABLE 3
Molecular Constants (in cm^{-1}) for the $a^3\Sigma_u^+$ State of He$_2$

| | $a^3\Sigma_u^+$ | | |
Constant	$v = 0$	$v = 1$	$v = 2$
T_v	0.	1732.1615(23)	3386.5024(60)
B_v	7.589141(27)	7.348742(32)	7.101747(120)
$D_v \times 10^4$	5.61529(136)	5.65381(178)	5.7439(70)
$H_v \times 10^8$	3.217(25)	2.837(30)	3.312(114)
$L_v \times 10^{12}$	-3.480(130)		
$\gamma_v \times 10^5$	-8.0805(22)	-7.5195(106)	-7.1466(67)
$\gamma_{Dv} \times 10^8$	2.2828(70)	1.9201(150)	1.946(32)
$\gamma_{Hv} \times 10^{12}$	-1.943(62)		
$\lambda_v \times 10^2$	-3.6664342(128)	-3.46179(28)	-3.25056(86)
$\lambda_{Dv} \times 10^6$	6.5887(37)	6.7549(40)	6.864(22)
$\lambda_{Hv} \times 10^{10}$	-1.595(94)	-1.595[a]	-1.595[a]
$\lambda_{Lv} \times 10^{14}$	4.65(62)	4.65[a]	4.65[a]

Note. All uncertainties are 1σ.
[a] Fixed.

TABLE 4
Molecular Constants (in cm^{-1}) for the $b^3\Pi_g$ State of He$_2$

| | $b^3\Pi_g$ | |
Constant	$v = 0$	$v = 1$
T_v	4768.14542(35)	6466.9837(23)
B_v	7.323430(29)	7.100611(34)
$D_v \times 10^4$	5.25315(161)	5.26152(202)
$H_v \times 10^8$	2.964(33)	2.762(36)
$L_v \times 10^{12}$	-2.51(21)	
A_v	-0.22733(82)	-0.22367(123)
$q_v \times 10^2$	-2.53917(94)	-2.47281(90)
$q_{Dv} \times 10^6$	5.189(62)	4.939(42)
$q_{Hv} \times 10^{10}$	-5.69(96)	
$p_v \times 10^4$	5.59(24)	6.65(38)
o_v	0.28975(37)	0.28835(48)
$\gamma_v \times 10^4$	-1.193(129)	-1.193[a]
$\lambda_v \times 10^2$	5.554(30)	5.361(38)

Note. All uncertainties are 1σ.
[a] Fixed.

TABLE 5
Molecular Constants (in cm^{-1}) for the $c^3\Sigma_g^+$ State of He$_2$

Constant	$c^3\Sigma_g^+$		
	v = 0	v = 1	v = 2
T_v	10889.4717(19)	12369.4987(25)	13741.2147(56)
B_v	6.853952(40)	6.556820(63)	6.226366(133)
$D_v \times 10^4$	5.58087(177)	5.8067(49)	6.3060(104)
$H_v \times 10^8$	2.221(28)	4.49(135)	6.5(30)
$L_v \times 10^{12}$	-7.523(139)	-3.68(120)	-4.49(29)
$\gamma_v \times 10^5$	-8.0805[a]	-8.0805[a]	-8.0805[a]
$\gamma_{Dv} \times 10^8$	2.2828[a]	2.2828[a]	2.2828[a]
$\lambda_v \times 10^2$	-3.6664342[a]	-3.6664342[a]	-3.6664342[a]
$\lambda_{Dv} \times 10^6$	6.5887[a]	6.5887[a]	6.5887[a]

Note. All uncertainties are 1σ.
[a] Fixed, see text.

The molecular constants derived from the fit for the $A^1\Sigma_u^+$, $B^1\Pi_g$, and $C^1\Sigma_g^+$ states are listed in Table 6 and the observed–calculated values for the FT lines are reported in parentheses in Table 2. In the final fit, the q_D parameter for the $B^1\Pi_g$ (v = 1) level was fixed to the corresponding value in the $B^1\Pi_g$ (v = 0) level because of the small amount of data available.

IV. DISCUSSION

The main goal of our work is to provide a consistent set of improved molecular constants for the six lowest excited states ($c^3\Sigma_g^+$, $b^3\Pi_g$, $a^3\Sigma_u^+$, $C^1\Sigma_g^+$, $B^1\Pi_g$, and $A^1\Sigma_u^+$) of He$_2$ based on modern laser and Fourier transform measurements of the line positions. The data for the infrared and near-infrared electronic transitions are augmented with the highly precise r.f. measurements of the fine structure splitting in the $a^3\Sigma_u^+$ state. Our molecular constants for v = 0, 1, and 2 of the $c^3\Sigma_g^+$ state (Table 5) and v = 0 and 1 of the $C^1\Sigma_g^+$ state (Table 6) are in good agreement with the previous results but are more than one order of magnitude more precise. The measurements of Ginter for the $c^3\Sigma_g^+$–$a^3\Sigma_u^+$ and $C^1\Sigma_g^+$–$A^1\Sigma_u^+$ systems (1), however, cover more vibrational levels (v = 0–3 for $A^1\Sigma_u^+$, v = 0–4 for $c^3\Sigma_g^+$, and v = 0–5 for $C^1\Sigma_g^+$). Substantial improvements,

particularly in the fine structure constants, were also made for v = 0, 1, and 2 in the $a^3\Sigma_u^+$ state. These improvements in the $a^3\Sigma_u^+$ constants help to break the correlation with the $b^3\Pi_g$ constants and our global fit thus refines the $b^3\Pi_g$ (v = 0 and 1) parameters.

The excited $c^3\Sigma_g^+$ state is influenced by both global and local perturbations. Hazell *et al.* (15) discuss the strong interaction of v = 2 of the $c^3\Sigma_g^+$ state with v = 6 of the $b^3\Pi_g$ state. This interaction results in peculiar spin splittings in the $c^3\Sigma_g^+$ v = 2 level as well as perturbed line positions. In our measurements we find that v = 1, N = 22 of the $c^3\Sigma_g^+$ state is also perturbed, probably by v = 5 of the $b^3\Pi_g$ state. The effect of $c \sim b$ interactions can also be seen in the erratic vibrational dependence of the effective H and L constants.

Improved equilibrium vibrational and rotational constants were derived by combining the new constants of Tables 3–6 with the more extensive (but less accurate) previous constants of Ginter and co-workers (2, 3, 6). For the $a^3\Sigma_u^+$ state, our v = 0–2 data were extended to v = 5 using Ref. (6) and equilibrium constants were derived (Table 7). A similar fit (v = 0–5) was carried out for the $A^1\Sigma_u^+$ state but in this case we were unable to determine any new vibrational intervals so we simply reproduce Ginter's vibrational constants (6) in Table 7. The $b^3\Pi_g$ and $B^1\Pi_g$ v = 0, 1 constants (Tables 4 and 6) were augmented by Ginter's v = 2 and 3 constants (2, 3). For the $b^3\Pi_g$ v = 2 and 3 constants we used the averages of the $b^3\Pi_g^+$ and $b^3\Pi_g^-$ values listed in Table IV of Ref. (3) (note that the $\Delta G_{3/2}$ and $\Delta G_{5/2}$ values for the $b^3\Pi_g^-$ component are erroneous, the values we assumed are $\Delta G_{3/2} = 1628.42 \pm 0.05$ cm^{-1} and $\Delta G_{5/2} = 1557.66 \pm 0.05$ cm^{-1}). For the $B^1\Pi_g$ v = 2 level we similarly used the averaged values from Ref. (2), while for the v = 3 level only the $B^1\Pi_g^-$ constants are available and they were accordingly deweighted in the fit. The $c^3\Sigma_g^+$ state shows the effects of perturbations by the $b^3\Pi_g$ state so that although data are available up to v = 5 (1, 13), we choose to make an exact fit of our new data. In this case the errors in Table 7 are not true statistical uncertainties but were estimated by the propagation of errors. For the $C^1\Sigma_g^+$ we report a $\Delta G_{1/2}$ value and an exact fit for the equilibrium rotational constants using

TABLE 6
Molecular Constants (in cm^{-1}) for the $A^1\Sigma_u^+$, $B^1\Pi_g$, and $C^1\Sigma_g^+$ Singlet States of He$_2$

Constant	$A^1\Sigma_u^+$		$B^1\Pi_g$		$C^1\Sigma_g^+$	
	v = 0	v = 1	v = 0	v = 1	v = 0	v = 1
T_v	0	1790.75[a]	3501.7970(9)	5198.7763(17)	10945.4772(15)	12517.2863(22)
B_v	7.671014(75)	7.446928(206)	7.287199(75)	7.067828(214)	6.947092(80)	6.699930(169)
$D_v \times 10^4$	5.4468(46)	5.437(24)	5.1850(41)	5.1358(159)	5.2025(49)	5.2495(125)
$H_v \times 10^8$	3.358(97)	1.75(108)	2.763(67)		2.590(103)	1.60(27)
$L_v \times 10^{12}$	-3.84(63)	3.34(167)			-4.00(69)	
$q_v \times 10^2$			-1.8125(19)	-1.7467(43)		
$q_{Dv} \times 10^6$			3.957(74)	3.957[b]		

Note. All uncertainties are 1σ.
[a] Fixed to the value from Ref. (1).
[b] Fixed.

TABLE 7
Equilibrium Constants (in cm^{-1} Unless Specified) for the $a^3\Sigma_u^+$, $A^1\Sigma_u^+$, $b^3\Pi_g$, $B^1\Pi_g$, $c^3\Sigma_g^+$, and $C^1\Sigma_g^+$ States of He$_2$

Constant	$a^3\Sigma_u^+$	$A^1\Sigma_u^+$	$b^3\Pi_g$	$B^1\Pi_g$	$c^3\Sigma_g^+$	$C^1\Sigma_g^+$
ω_e[a]	1808.500(84)	[1861.3][c]	1769.337(60)	1766.151(19)	1588.338(16)	[1571.8091(37)][d]
$\omega_e x_e$	37.812(75)	[35.2][c]	35.249(29)	34.586(10)	54.1555(60)	
$\omega_e y_e$	-0.197(25)	[-0.13][c]				
$\omega_e z_e$	-0.0145(26)					
B_e[b]	7.707364(67)	7.78140(26)	7.433442(79)	7.39548(36)	6.99002(20)	7.07067(20)
α_e	0.234(16)	0.21974(52)	0.21909(21)	0.21561(92)	0.26381(40)	0.24716(25)
$\gamma_{1e}\times10^3$	-2.11(14)	-2.10(17)	-1.86(10)	-1.88(44)	-16.66(15)	
$\gamma_{2e}\times10^4$	-2.65(28)					
R_e (Å)	1.0454158(45)	1.040431(17)	1.0645033(56)	1.067232(26)	1.097748(16)	1.091470(15)

Note. All uncertainties are 1σ.

[a] $G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4$.

[b] $B(v) = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_{1e}(v + \frac{1}{2})^2 + \gamma_{2e}(v + \frac{1}{2})^3$.

[c] From Ref. (6).

[d] $\Delta G_{1/2}$ value.

the data of Table 6. New R_e values were then calculated from B_e and are also reported in Table 7.

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