

5. DISCUSSION

We have demonstrated the wide applicability of the Green's function methods for the study of sequential decay problems involving interference between continua. The most interesting physical results emerging from the present treatment involve the retardation of the decay of the initially optically excited state due to interference effects and the effects of interference on the population of the dissipative coupled continua.

From the physical point of view these theoretical models may be of interest for the elucidation of the features of multistage photo-fragmentation processes. In this case an initially optically excited state of a large molecule decays into an intramolecular dense quasi-continuum of highly excited bound vibronic levels (corresponding to a lower electronic configuration). These highly excited vibronic levels (corresponding to a low electronically excited state) may then subsequently decay into a dissociative continuum by predissociation. Under these conditions the role of interference effects may be crucial in determining the details of the photofragmentation reactions [8].

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Ab initio calculation of the He, $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ absorption spectrum

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The absorption spectrum of helium gas near 600 Å, assigned to the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition in He₂, is calculated at 77 K. The excited state potential is taken from a recent *ab initio* calculation. The theoretical spectrum shows well-defined bands, corresponding to different vibration levels of the *A* state, with diffuse rotational structure, in agreement with experiment. Fairly good quantitative agreement with Tanaka and Yoshino's measured spectrum is obtained, except for the somewhat too large separation between calculated vibrational bands, probably due to the theoretical potential for the *A* state rising too steeply at small inter-nuclear separation. Rotational constants derived from the calculated and experimental spectra are in good agreement. It is shown that they are significantly smaller than actual rotational constants of the upper state.

1. INTRODUCTION

We have recently reported an *ab initio* potential for the lowest excited singlet state of the He₂ molecule, the $A^1\Sigma_u^+$ state, and obtained very good agreement of molecular constants, especially those depending on the shape of the potential near its minimum, with experiment [1]. Much of the interest in this state, as well as our knowledge of it, results from transitions connecting it with the $X^1\Sigma_g^+$ ground state. The 600 Å bands in the helium gas absorption spectrum†, assigned to the $A \leftarrow X$ transition, have been measured by Tanaka and Yoshino [2], and later by Chow *et al.* [3]. Tanaka and Yoshino carried out high-resolution studies of the absorption spectrum at 77 K, and observed six bands originating from different vibrational levels of the *A* state. Diffuse rotational structure was also found.

Sando and Dalgarno [4] obtained a theoretical spectrum in good agreement with experiment by modifying the *A* state potential until it reproduced the experimental spectrum. In this paper we report an *ab initio* calculation of the 600 Å absorption bands, using our previously reported potential for the $A^1\Sigma_u^+$ state.

2. METHOD

The electric dipole transition probability (per unit energy) at energy *E* associated with absorption from state $|i\rangle$ to $|f\rangle$ is proportional to

$$A_{if}(E) = E \langle i | \mu | f \rangle^2, \quad (1)$$

$$\dagger A = 10^{-16} \text{ m.}$$

where μ is the dipole moment operator. Invoking the Born-Oppenheimer approximation we write

$$|f\rangle = \phi(\mathbf{r}, R) \chi_{v,J'}(R) R^{-1} Y_{J',M'}(\mathbf{R}/R), \quad (2)$$

where the three functions on the right-hand side are the electronic, vibrational and rotational functions, \mathbf{r} represents the electronic coordinates, and \mathbf{R} is the vector joining the two nuclei. The continuous set of eigenfunctions for the repulsive initial state is given by

$$|i\rangle = \phi_i(\mathbf{r}, R) \chi_{v_i,J_i}(R) R^{-1} Y_{J_i,M_i}(\mathbf{R}/R). \quad (3)$$

To obtain the total absorption probability per unit energy E we sum over all pairs of initial and final states separated by E , taking into account the population of the initial states:

$$A(E) \sim \sum_{E_i - E_f = E} A_{if}(E) \exp(-E_i/kT). \quad (4)$$

Substituting expressions (2) and (3) and applying the selection rules on J and M we get

$$A(E) \sim E \sum_{v_i, v_f} (2J_f + 1) |F_{v_i, v_f}(E)|^2 \exp(-E_i/kT) \quad (5)$$

where the Franck-Condon factor F_{v_i, v_f} is

$$F_{v_i, v_f} = \int_0^\infty \chi_{v_i, v_f} \chi_{v_i, v_f}^* \chi_{v_i, v_f} dR \quad (6)$$

and

$$E_i = E_{v_i, J_i} - E. \quad (7)$$

Two simplifying assumptions are incorporated in equation (5). The first one, the weak dependence of the electronic transition dipole

$$\mu_{if}(R) = \int \phi_i \mu \phi_f d\mathbf{r} \quad (8)$$

on R (in the range contributing to the transition) is generally used [5] and has specifically been shown to apply in our case [6]. The second simplification involves the Franck-Condon factor of equation (6). An application of the

J selection rules yields the integrals $\int_0^\infty \chi_{v_i, v_f} \chi_{v_i, v_f}^* \chi_{v_i, v_f} dR$, but we found that substituting the more convenient F_{v_i, v_f} causes only negligible change.

The nuclear functions needed are obtained by solving the equation

$$\frac{1}{2M} \frac{d^2 \chi}{dR^2} + \left[E - U(R) - \frac{J(J+1)}{2MR^2} \right] \chi = 0 \quad (9)$$

with appropriate electronic potentials $U(R)$ and boundary conditions. M is the reduced mass of the nuclei. The 'adjusted potential' of Klein *et al.* [7] was taken for the ground state, and the energy-normalized continuum functions were obtained by Numerov integration of equation (9) [8]. Our CI-209

potential [1] was used for the $A^1\Sigma_u^+$ state, and the $X_{v,J'}$ functions were calculated by expansion in a harmonic oscillator basis [9]. The two quasi-bound levels were treated in the same manner [1, 10]. The A potential was shifted down by 0.0234 a.u. (5120 cm⁻¹) to adjust its height above the ground state at infinite separation to the value corresponding to the atomic helium $(1s)(2s)1S + (1s)^21S$ transition.

3. RESULTS AND DISCUSSION

The calculated $X \rightarrow A$ absorption spectrum at 77 K appears in figure 1. It shows the well-defined vibrational bands found experimentally [2]. A larger-scale picture of band III exhibits the partly-resolved rotational structure, also

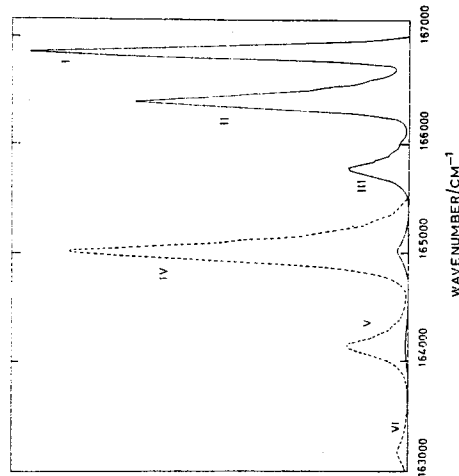


Figure 1. The calculated absorption spectrum at 77 K. The dashed line includes a multiplication factor of 30.

in qualitative agreement with experiment. The quantitative comparison of calculated energies and intensities of absorption maxima with Tanaka and Yoshino's [2] results show reasonably good agreement (table 1), the main discrepancy being the too large separation of the calculated vibration levels. A related problem is the number of vibration levels supported by the A state. Tanaka and Yoshino suggest 15 levels, while Smith and Chow [11] claim 17 levels and Sando [12] obtains 18 levels. The He₂⁺ calculations of Liu [13] seem to support Sando's value. Our CI-209 potential accommodates 16 levels (two of them quasi-bound, corresponding to the two absorption bands at energies

higher than the atomic transition). On comparison with Sando's empirical potential [12] it seems that the main deficiency of the CI-209 potential is rising too fast at small inter-nuclear separation ($< 0.75 \text{ \AA}$); a flatter potential would yield more and closer vibrational levels.

Band	v'	J'	Transition wavenumber/cm ⁻¹		Line intensity		Band intensity	
			Calculated	Exp. [2]	Calculated	Exp. [2]	Calculated	Exp. [2]
I	15	1	166846	166655	10	10	1000	1000
		3	166856	166663	11	10		
		5	166886		9			
		7	166921		6			
II	14	1	166374	166372	10	10	690	200
		3	166395	166389	11	9		
		5	166433	166422	9	6		
		7	166481	166466	5	3		
		9	166551		2			
III	13	1	165740	165902	10	10	150	50
		3	165765	165927	11	9		
		5	165810	165968	9	8		
		7	165875	166026	5	5		
		9	165960	166101	2	2		
		1	164978	165301	10	10	29	10
		3	165008	165328	11	9		
IV	12	1	165088	165375	9	7		
		3	165133	165445	5	5		
		5	165233	165535	2	2		
		7	164104	164586	10	10	5	5
		9	164134	164620	11	9		
		1	164194	164676	9	6		
		3	164284	164752	4	4		
V	11	1	164394	164859	1	1	1	2
		3	163130	163740	10	10		
		5	163162		11			
		7	163231		8			
		9	163323		4			

Table 1. He₂ absorption maxima at 77 K.

Band	Calculated		Experimental [2]
	from potential [1]	from spectrum	
I	2.65	1.39	0.83
II	3.31	2.02	1.74-2.06
III	3.83	2.50	2.29-2.53
IV	4.26	2.89	2.67-2.99
V	4.64	3.27	3.16-3.46
VI	4.99	3.58	

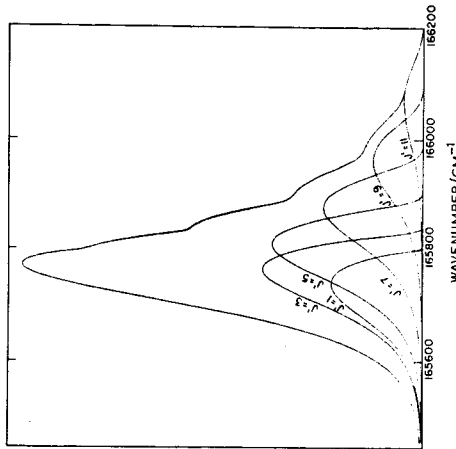
Table 2. Rotational constants B_v/cm^{-1} .

Figure 2. Band III at 77 K. The lower curves show absorption to individual rotation levels of the A state, and the upper curve is the total absorption.

We have noted [1] that while the rotational constants yielded by the CI-209 potential for the lower vibrational levels of the A state were in very good agreement with Ginter's experimental values [14], no such agreement was found with Tanaka and Yoshino's results [2] for the higher levels. We would like to point out that the B_v values quoted by Tanaka and Yoshino do not correspond directly to rotational energies in the A state. The effective potential of the ground state is also J -dependent (see equation (9)); an absorption to a higher rotational level of the excited state starts therefore from a higher ground-state potential, and the difference between energies of absorption to two adjacent rotational levels is smaller than their actual separation. Rotational constants derived from the theoretical spectrum are shown in table 2 to be lower than corresponding constants obtained directly from the potential and in good agreement with experimental values.

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