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# Continuum resonance Raman scattering of light by diatomic molecules. II. Theoretical study of the $Q$ branches of $\Delta n = 1$ profiles of molecular bromine<sup>a)</sup>

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The methods developed in Part I for the calculation of continuum resonance Raman scattering amplitudes are applied to the calculation of the  $Q$  branches of the  $\Delta n = 1$  profiles of  $\text{Br}_2$  which have been measured by Baierl and Kiefer [J. Raman Spectrosc. 3, 353 (1975)]. The experimental conditions being such as to imply many initial and final rovibrational states, we first of all study the effect of rotation on the scattering amplitudes. It is observed that while the amplitudes may vary substantially with the rotational number of the initial state, almost no effect is introduced by taking into account the changes in rotational quantum numbers which accompany transitions between different electronic states. This is useful to derive an efficient formula for the scattering cross section. The profiles are then calculated with the potentials available for the  $^1\Pi_{1u}$  and  $B(^3\Pi_{0u}^+)$  excited states which, as shown by previous workers, interfere strongly in producing the spectra. These calculations make it possible to examine the effect of (1) using semiclassical scattering amplitudes rather than the more accurate coupled channel results, (2) using  $R$ -dependent electronic transition moments instead of constant ones, (3) introducing the effect of the angular momentum quantum number  $J$  instead of using the amplitudes calculated for  $J = 0$ , (4) choosing the potentials among those derived from absorption data. The conclusions which emerge from these calculations are that: (a) The semiclassical procedure is fairly accurate. This success indicates that a Raman profile for a given exciting wavelength represents in fact a very local test (over a range of  $\sim 0.03$  Å) of the excited states potentials. Changing the wavelength from 5017 to 4579 Å (two of the lines available from an argon ion laser) amounts to scanning each of the potentials over a region of no more than 0.1 Å; (b) The changes in the scattering amplitudes brought about by the introduction of varying electronic transition moments can be correlated with the values taken by the moments at the radiative crossing points. This is supported both by a detailed analysis of the coupled channel amplitudes and by the form taken by the semiclassical amplitudes; (c) The effect of  $J$  on the amplitudes is masked in the profiles as a result of superposition effects; (d) None of the published potentials was able to fit all five profiles. A local downward displacement of the potentials for the  $^1\Pi_{1u}$  and  $B(^3\Pi_{0u}^+)$  states removes the main unsatisfactory features of the spectra.

## I. INTRODUCTION

Resonance Raman spectra of diatomic molecules in the gas phase present a rather complicated structure due to the superposition of many distinct transitions<sup>1,2</sup> which result from the fact that in the usual conditions of the experimental measurements<sup>3</sup> the temperature is such that many initial rovibrational states are populated. The structure of the spectrum reflects the properties of the ground electronic state (anharmonic and rotational spacings), but to account for the intensities it is necessary to make a choice for the potentials of the excited states. A theoretical fitting of the spectra therefore constitutes a method for deriving these potentials, and this has already been done for molecular iodine and bromine.<sup>4,5</sup> We again take up the case of the bromine molecule in this paper in order to assess the usefulness of the methods given in Paper I. With the potentials available in the literature we have been unable to reproduce in a satisfactory way all five experimental profiles. With a local downward displacement it was possible to

annihilate some undesirable features in the spectra. In the process of attempting such fits we have been looking in turn at the effects of introducing the rotation of the molecule and of using varying electronic transition moments.

## II. THE EFFECT OF ROTATION ON CONTINUUM RESONANCE RAMAN SCATTERING AMPLITUDES. DIFFERENTIAL CROSS SECTIONS

It is well known that rotation may affect significantly the level widths of predissociating levels.<sup>6</sup> Thus we may expect that introducing centrifugal energies into the molecular potentials will produce some effect on Raman scattering amplitudes because of the analogies between the two problems. The effect of rotation has only been very briefly mentioned previously,<sup>2</sup> and it was proposed that this could be accounted for by a relative displacement of the potentials in order to take into account the differences in the two states of the centrifugal energies calculated at the equilibrium distance of the bound state. Our findings, to be described below, indicate that the changes in rotational quantum numbers which accompany an electronic transition produce only very small effects, but that significant variations with the rotational quantum number of the initial state may

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<sup>b)</sup>Laboratoire du C. N. R. S. .

TABLE I. Effect of angular quantum numbers on scattering amplitudes (in cm) via the  $^1\Pi$  state of  $\text{Br}_2$  with Coxon's potential.<sup>7b</sup> Coupled equations (C. E.) are used when  $\Delta J = 0$ . Semiclassical (S. C.) formulas are used for  $\Delta J = 0, \pm 1$ .

$n'$	$n''$	$J''$	$\Delta J$	$\Gamma_{n', J'', J, n'', J''}$		$\Delta_{n', J'', J, n'', J''}$		$ I_{n', J'', J, n'', J''} ^2$	
				C. E.	S. C.	C. E.	S. C.	C. E.	S. C.
0	1	0	0	0.2874-4	0.2847-4	0.1443-3	0.1468-3	0.2164-7	0.2237-7
0	1	0	+1		0.2846-4		0.1468-3		0.2236-7
0	1	10	-1		0.2814-4		0.1464-3		0.2222-7
0	1	10	0	0.2875-4	0.2804-4	0.1422-3	0.1463-3	0.2104-7	0.2218-7
0	1	10	+1		0.2793-4		0.1461-3		0.2213-7
0	1	30	-1		0.2527-4		0.1424-3		0.2092-7
0	1	30	0	0.2639-4	0.2499-4	0.1405-3	0.1420-3	0.2042-7	0.2077-7
0	1	30	+1		0.2471-4		0.1415-3		0.2063-7
0	1	50	-1		0.2011-4		0.1343-3		0.1844-7
0	1	50	0	0.2089-4	0.1973-4	0.1321-3	0.1337-3	0.1790-7	0.1825-7
0	1	50	+1		0.1934-4		0.1330-3		0.1806-7
0	1	70	-1		0.1394-4		0.1228-3		0.1527-7
0	1	70	0	0.1404-4	0.1354-4	0.1192-3	0.1219-3	0.1440-7	0.1505-7
0	1	70	+1		0.1315-4		0.1211-3		0.1484-7
1	2	0	0	0.1861-3	0.1867-3	0.2725-3	0.2788-3	0.1089-6	0.1126-6
1	2	0	+1		0.1866-3		0.2788-3		0.1125-6
1	2	10	-1		0.1851-3		0.2786-3		0.1188-6
1	2	10	0	0.1818-3	0.1846-3	0.2614-3	0.2785-3	0.1014-6	0.1117-6
1	2	10	+1		0.1841-3		0.2784-3		0.1140-6
1	2	30	-1		0.1712-3		0.2760-3		0.1055-6
1	2	30	0	0.1721-3	0.1698-3	0.2750-3	0.2757-3	0.1053-6	0.1048-6
1	2	30	+1		0.1683-3		0.2754-3		0.1042-6
1	2	50	-1		0.1445-3		0.2689-3		0.9319-7
1	2	50	0	0.1447-3	0.1424-3	0.2671-3	0.2681-3	0.9230-7	0.9218-7
1	2	50	+1		0.1403-3		0.2674-3		0.9119-7
1	2	70	-1		0.1092-3		0.2542-3		0.7654-7
1	2	70	0	0.1061-3	0.1068-3	0.2417-3	0.2529-3	0.6969-7	0.7534-7
1	2	70	+1		0.1044-3		0.2515-3		0.7415-7

occur. This is the justification for the approximation made in Paper I when deriving an expression for the scattering amplitude with the angles being integrated out.

The calculations which are presented in Table I have been done in the course of the investigation of the resonance Raman profiles of  $\text{Br}_2$ , to be described in more detail in the following sections. Both coupled channel equations and semiclassical formulas were used. The case which is considered is scattering via the  $^1\Pi$  state of  $\text{Br}_2$ , the potentials of the ground state and of the excited state being taken from the work of Coxon.<sup>7b</sup> Amplitudes have been calculated for  $J'' = J' = 0, 10, 30, 50, 70$  and  $\Delta J = 0, \pm 1$ , with  $n' = n'' + 1$  and  $n'' = 0$  or 1. In the conditions of the experimental measurements<sup>3</sup> the absolute temperature is around 700 K, corresponding to  $J_{\text{max}} \sim 50$ . The collision energy  $\bar{E}$  is  $20\,500\text{ cm}^{-1}$ . Coupled equations are used only when  $\Delta J = 0$ , but the good agreement obtained for this case with the semiclassical results indicates once more that the latter method is reliable and makes it possible to study the changes in the amplitudes when  $\Delta J \neq 0$ . The columns giving  $|I_{n', J'', J, n'', J''}|^2$  show that while changing the rotational quantum number of the initial state from 0 to 70 there is a change of about 50% in the state-to-state cross section, the numbers belonging to the same triplets (i. e., numbers corresponding to  $\Delta J = 0, \pm 1$ ) are very similar since the changes now represent only a few percent.

In the calculations made below we have either ignored the effect of  $J$  (this implying  $J = 0$ ) on the vibrational functions, or taken into account this effect but with  $J = J''$  for all the vibrational functions affecting a given amplitude. When in the following we speak of the effect of rotation, this means introducing it in this manner. It must be emphasized that this does not imply any approximation in the manipulation of the rotational functions.

We now complete our derivation of a differential cross section which was stopped in Paper I at the point where we could define the amplitudes to be obtained from a reduced set of coupled equations. We recall the formula [Eq. (42) of Paper I]

$$A_{n', J'', J, n'', J''}^{J', J', J', J'}(\bar{E}) = \left( \frac{2J'' + 1}{2J' + 1} \right)^{1/2} \sum_{j=0}^2 C_j(\bar{E}) \times \langle J'' J M'' | \xi + \eta | J' M' \rangle \langle 11 \xi \xi | j \xi + \eta \rangle \langle J' J 00 | J' 0 \rangle. \quad (1)$$

According to Ref. 8, we can define the following averages:

$$\begin{aligned} \langle A_{n', J'', J, n'', J''}^{J', J', J', J'} \rangle_{n', J'', J, n'', J''} &= \frac{N_{n', J''}}{2J'' + 1} \sum_{M', M''} A_{n', J'', J, n'', J''}^{J', J', J', J'}(\bar{E}) \\ &\times A_{n', J'', J, n'', J''}^{J', J', J', J'}(\bar{E}) = N_{n', J''} \sum_{j=0}^2 \frac{|C_j|^2}{2j + 1} \\ &\times \langle 11 \xi \xi | j \xi + \eta \rangle \langle J' J 00 | J' 0 \rangle^2 \delta_{J', J'', J', J''}, \end{aligned} \quad (2)$$

where  $N_{n',j'',n'',j''}$  is the Boltzmann population of the initial state. The state-to-state right angle differential cross section corresponding to an experiment with incoming photons linearly polarized along  $Z$  and observation in the  $Y$  direction is proportional to

$$\frac{d\sigma}{d\Omega}(n'j',n''j'') \propto \langle |A^{ZZ}|^2 \rangle_{n'j',n''j''} + \langle |A^{YZ}|^2 \rangle_{n'j',n''j''} . \quad (3)$$

We have the relations

$$A_{n'j',n''j''}^{ZZ}(\bar{E}) = A_{n'j',n''j''}^{00}(\bar{E}) \quad (4)$$

and

$$A_{n'j',n''j''}^{YZ}(\bar{E}) = \frac{i}{\sqrt{2}} [A_{n'j',n''j''}^{10}(\bar{E}) + A_{n'j',n''j''}^{10}(\bar{E})] , \quad (5)$$

which can serve to express the averages found in Eq. (3) in terms of those defined by Eq. (2). Performing this operation leads for the differential cross section to

$$\begin{aligned} \frac{d\sigma}{d\Omega}(n'j',n''j'') &\propto N_{n'j',n''j''} \left[ \frac{1}{2} |C_0|^2 \langle J''000 | J'0 \rangle^2 \right. \\ &\quad + \frac{1}{6} |C_1|^2 \langle J''100 | J'0 \rangle^2 \\ &\quad \left. + \frac{7}{30} |C_2|^2 \langle J''200 | J'0 \rangle^2 \right] . \quad (6) \end{aligned}$$

The calculations which will be performed concern the  $Q$  branch ( $J' = J''$ ). In this case Eq. (6) takes the form

$$\begin{aligned} \frac{d\sigma}{d\Omega}(n'j'',n''j'') &\propto N_{n'j'',n''j''} \\ &\times \left[ \frac{1}{3} |C_0|^2 + \frac{7}{30} \frac{J''(J''+1)}{(2J''-1)(2J''+3)} |C_2|^2 \right] . \quad (7) \end{aligned}$$

This is the formula used in the calculation of the profiles.  $C_0$  and  $C_2$  are obtained from

$$\begin{aligned} C_0 &= \frac{-1}{\sqrt{3}} [\bar{\alpha}_{n'j'',n''j''}^{00}(\bar{E}) - \bar{\alpha}_{n'j'',n''j''}^{11}(\bar{E}) \\ &\quad - \bar{\alpha}_{n'j'',n''j''}^{1-1}(\bar{E})] , \quad (8) \\ C_2 &= \frac{1}{\sqrt{6}} [\bar{\alpha}_{n'j'',n''j''}^{11}(\bar{E}) + \bar{\alpha}_{n'j'',n''j''}^{1-1}(\bar{E}) \\ &\quad + 2\bar{\alpha}_{n'j'',n''j''}^{00}(\bar{E})] . \quad (9) \end{aligned}$$

The  $\bar{\alpha}_{n'j'',n''j''}^{\xi\xi}(\bar{E})$ 's have been defined in Eq. (41) of Paper I.

### III. POTENTIALS AND TRANSITION MOMENTS OF THE BROMINE MOLECULE

The absorption spectrum of the bromine molecule in the region 18 000–28 000 Å results from transitions towards both the  ${}^1\Pi_{1u}$  and  $B({}^3\Pi_{0u}^+)$  states. The two states will be abbreviated in the following as  ${}^1\Pi$  and  ${}^3\Pi$ . This was recognized a long time ago by Acton, Aickin, and Bayliss.<sup>9</sup> An analysis of this spectrum by Bayliss<sup>10</sup> led him to propose for the potential of the  ${}^1\Pi$  state the form

$$V_{1\Pi}^B(R) = A + B/R^2 , \quad (10)$$

with  $A = -0.400953 \times 10^5 \text{ cm}^{-1}$ ,  $B = 0.25213 \times 10^6 \text{ cm}^{-1}/\text{\AA}^2$ .

More recently, Barrow *et al.*<sup>7a</sup> and Coxon<sup>7b</sup> have re-analyzed the absorption data and obtained the two poten-

tials for the  ${}^1\Pi$  and  ${}^3\Pi$  states in a form which is partly numerical and partly analytical. The analytical form represents a mean of extrapolating the potentials outside the region which is meaningful for the absorption. Thus, for  ${}^1\Pi$  the potential is given numerically for  $1.55 \text{ \AA} \leq R \leq 7.475 \text{ \AA}$ , while for  ${}^3\Pi$  this interval is  $1.55 \text{ \AA} \leq R \leq 4.85 \text{ \AA}$ . As we shall see, the regions which matter for Raman scattering are also within these intervals.

Finally, LeRoy, Macdonald, and Burns<sup>11</sup> have used a least square fitting procedure with the purpose of determining from the absorption data both the potentials of the two excited states and the  $R$ -dependent electronic transition moments. For the  ${}^1\Pi$  state, for  $2.10 \text{ \AA} \leq R \leq 2.55 \text{ \AA}$  the potential is (in  $\text{cm}^{-1}$ )

$$V_{1\Pi}^L(R) = 16\,056.9 + 7654 \times \exp[-4.367(R-2.3) - 0.879(R-2.3)^2] , \quad (11)$$

and the transition moment (in debye)

$$D_{1\Pi}^L(R) = 0.5060 - 0.154(R-2.3) . \quad (12)$$

For the  ${}^3\Pi$  state for  $2.10 \text{ \AA} < R < 2.55 \text{ \AA}$  the potential is

$$V_{3\Pi}^L(R) = 14\,882.2 + 5494 \exp[-5.807(R-2.3)] , \quad (13)$$

and the transition moment

$$D_{3\Pi}^L(R) = 0.3905 + 0.265(R-2.3) . \quad (14)$$

The profiles to be calculated correspond to the exciting wavelengths used by Baierl and Kiefer,<sup>3</sup> that is,

$$\begin{aligned} \lambda_1 &= 5017 \text{ \AA}; \quad \lambda_2 = 4965 \text{ \AA}; \\ \lambda_3 &= 4880 \text{ \AA}; \quad \lambda_4 = 4765 \text{ \AA}; \quad \lambda_5 = 4579 \text{ \AA} . \end{aligned}$$

The potentials introduced into the profile calculations are as follows: (a) the Bayliss potential<sup>10</sup> for the  ${}^1\Pi$  state in conjunction with the Coxon potential<sup>7b</sup> for the  ${}^3\Pi$  state. This choice will be designated as Bayliss-Coxon; (b) The Coxon potentials<sup>7b</sup> for both  ${}^1\Pi$  and  ${}^3\Pi$  states, with eventually an overall vertical translation for reasons to be given below; (c) The LeRoy potentials<sup>11</sup> for both  ${}^1\Pi$  and  ${}^3\Pi$  states; (d) a Morse potential for the ground state with

$$\omega_e = 323.28 \text{ cm}^{-1}; \quad \omega_e x_e = 1.07 \text{ cm}^{-1} .$$

The potentials given in Eqs. (10), (11), and (13) have their origins at the minimum of the ground state potential. The reduced mass is that of the  ${}^{79}\text{Br}^{81}\text{Br}$  isotope ( $\mu = 39.3524 \text{ amu}$ ).

Some calculations are done with constant electronic transitions moments. Other calculations are done with  $D_{1\Pi}^L(R)$  and  $D_{3\Pi}^L(R)$  as given by Eqs. (12) and (14).

### IV. ROTATIONLESS PROFILE CALCULATIONS

The first series of calculations has been performed with no centrifugal energies in the potentials. Coupled equations were used since a limited number of scattering amplitudes is needed in this case. The temperature is taken equal to 700 K. The spectra being the superposition of a large number of distinct lines, the profiles are obtained by summing up for a given frequency the

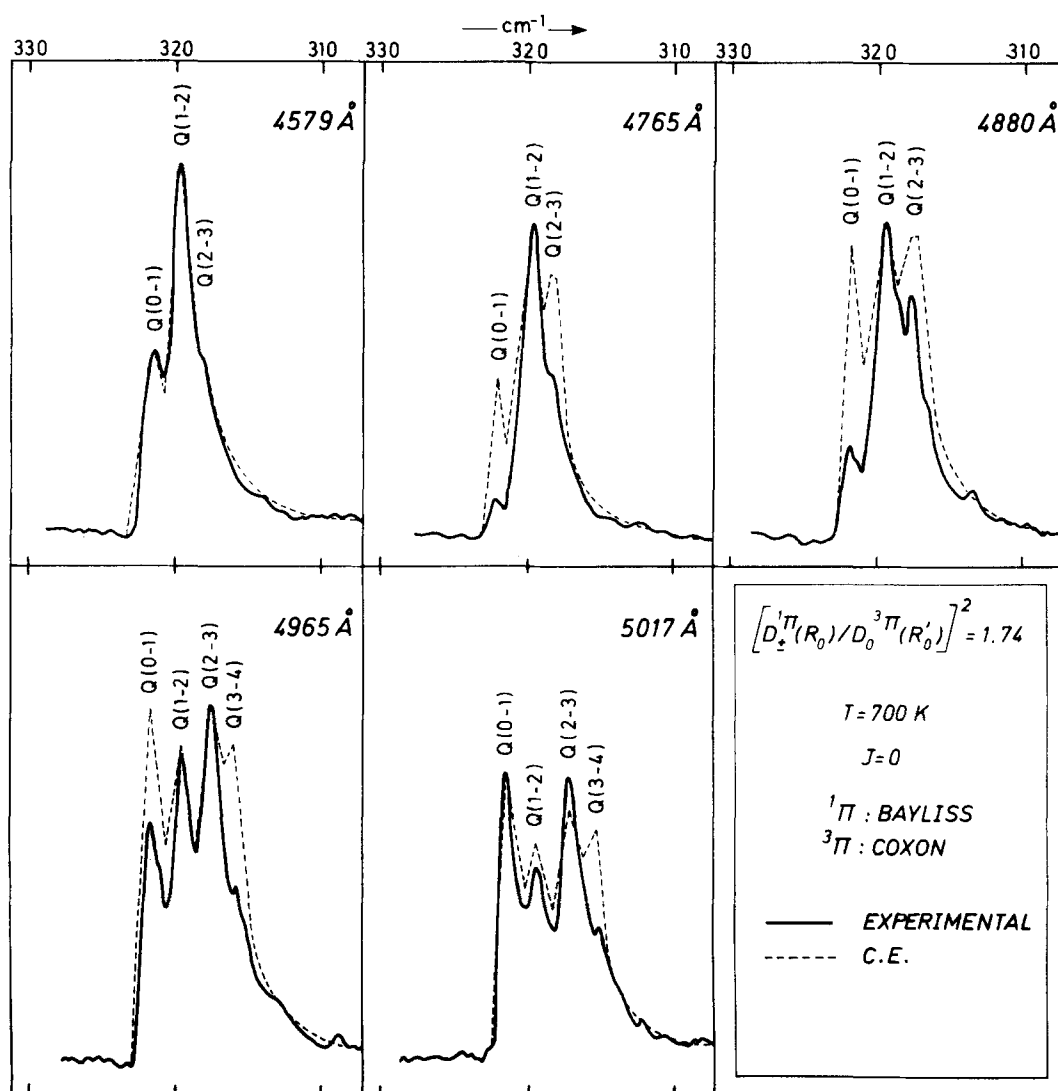


FIG. 1. Experimental and calculated (coupled equations) profiles with Bayliss potential<sup>10</sup> for the  $^1\Pi$  state and Coxon's potential<sup>7b</sup> for the  $^3\Pi$  state.  $R_0$  and  $R'_0$  may be considered as internuclear distances within the effective range of each potential. The intensities are in arbitrary units.

intensities of all the lines within an interval of  $1\text{ cm}^{-1}$  around this frequency. This amounts to a convolution with a rectangular slit  $1\text{ cm}^{-1}$  wide. This procedure has been followed in all calculations presented here. The important informations are the ratios of peak intensities. These peaks are associated with the different initial vibrational quantum numbers. Their separations reflect the anharmonicity of the ground state. They are labelled  $Q(n' - n'')$ .

Figure 1 gives the five profiles calculated with the Bayliss-Coxon<sup>7b,10</sup> potentials and constant electronic transition moments, together with the experimental profiles. The ratio of the squared electronic transition moments is 1.74. The calculations account for the decreasing complexity of the profiles when increasing the photon frequency. The 4579 Å profile which shows only two peaks is very well reproduced, but as we shall see this profile is not very sensitive to the choice of potentials. We have checked on this profile the interference effect discovered by Baierl, Kiefer, Williams, and Rousseau<sup>5</sup> and obtained very similar results. The 4765

and 4880 Å profiles are both characterized by relatively too intense  $Q(1-0)$  and  $Q(3-2)$  peaks. In the 4965 and 5017 Å profiles, it is the  $Q(4-3)$  peak which is relatively too intense. There are other dissatisfying features, but we already note a general trend. Decreasing the photon frequency produces, as in the experimental profiles, the emergence of peaks corresponding to higher initial quantum numbers, but this occurs too soon and with too high relative intensities.

In Fig. 2, the potentials are those of Coxon<sup>7b</sup> for both  $^1\Pi$  and  $^3\Pi$  states. The profiles are calculated with either the same ratio as in Fig. 1 for the transition moments or the transition moments of LeRoy *et al.*<sup>11</sup> The results are less satisfactory than for the Bayliss-Coxon combination. The new peaks appearing in the spectra when lowering the photon frequency [ $Q(3-2)$  in the 4765 Å profile, both  $Q(3-2)$  and  $Q(4-3)$  in the 4880 Å profile, and  $Q(4-3)$  in the 4965 and 5017 Å profiles] are enhanced considerably. As to the effect of introducing the variation of the transition moments, we note that the relative intensities are only slightly modified, with

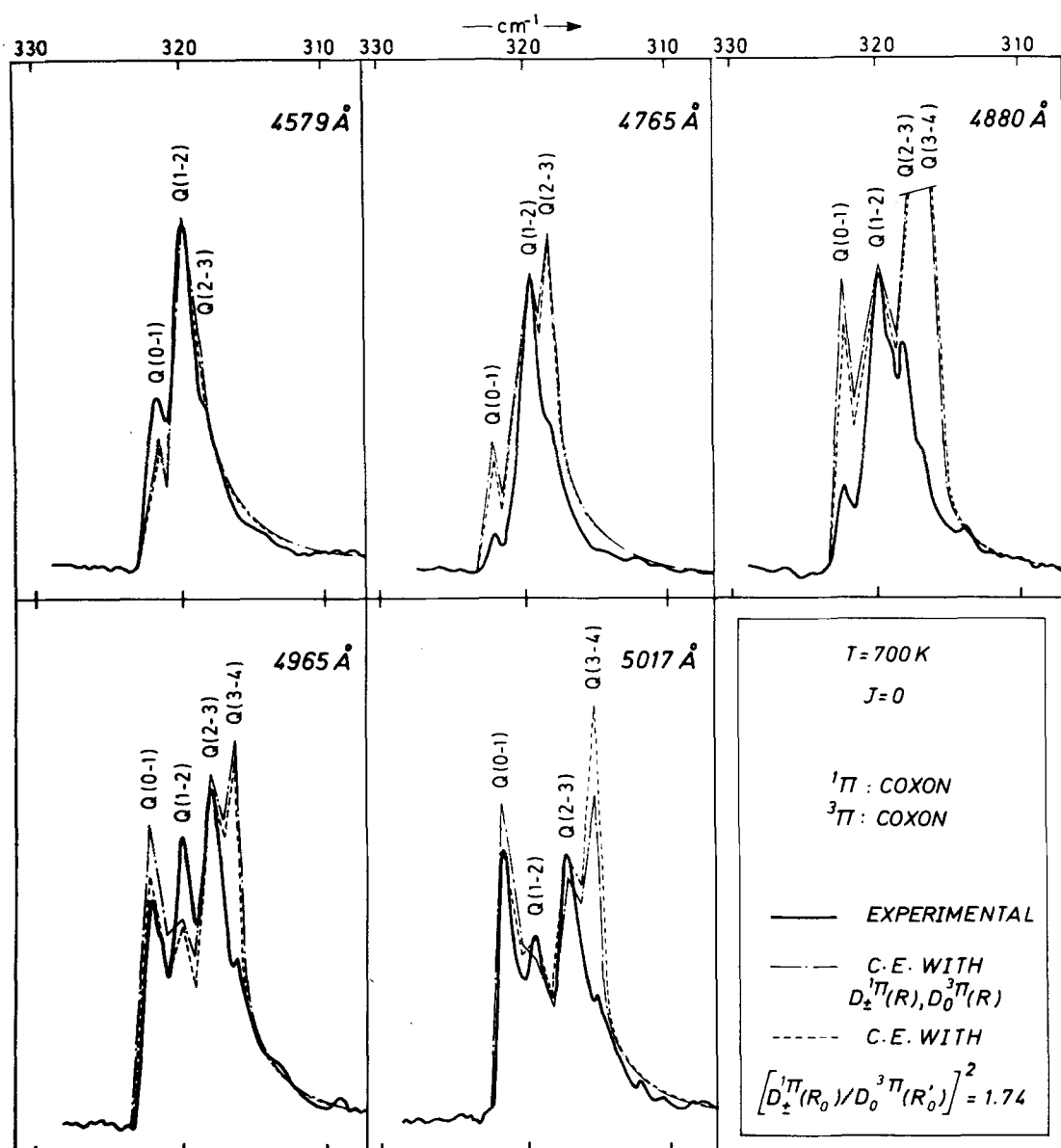


FIG. 2. Experimental and calculated (coupled equations) profiles with Coxon's potentials<sup>7b</sup> with and without  $R$  dependence of the electronic transition moments.

the exception of the  $Q(1-0)$  peaks in the 4965 and 5017 Å spectra, which are somewhat enhanced.

The set of spectra shown in Fig. 3 are calculated with LeRoy's potentials<sup>11</sup> with, again, either constant or varying electronic transition moments. These spectra are in fact very similar to those of Fig. 2, with the same defects and the same rather minor changes when introducing the variation in the transition moments.

To conclude the examination of these series, it appears that the theoretical profiles calculated with  $J=0$  and constant electronic transition moments have some unsatisfactory features which are not corrected by the introduction of the  $R$  dependence of the transition moments.

## V. SEMICLASSICAL PROFILE CALCULATIONS

In Sec. VI, we shall investigate the effect of rotation on the scattering amplitudes as a potential source of

improvement since, as shown in Sec. II, the centrifugal energy may sometimes affect strongly the amplitudes. Because such calculations require a large number of amplitudes, we first of all examine whether we could replace the coupled channel results by their semiclassical counterparts. Table II gives for the Coxon potentials the real and imaginary parts of all the amplitudes up to  $n''=3$ ;  $n'=4$ , for the five exciting wavelengths, for both the coupled channel and semiclassical methods. There is good overall agreement between the two procedures. The largest disagreements are observed when both methods are producing numbers smaller than the average.

Figure 4 gives the five profiles calculated with the amplitudes of Table II. These were not drawn on the same figure as the coupled channel profiles because they are in fact almost indistinguishable. The only serious discrepancy is observed in the 5017 Å profile where the

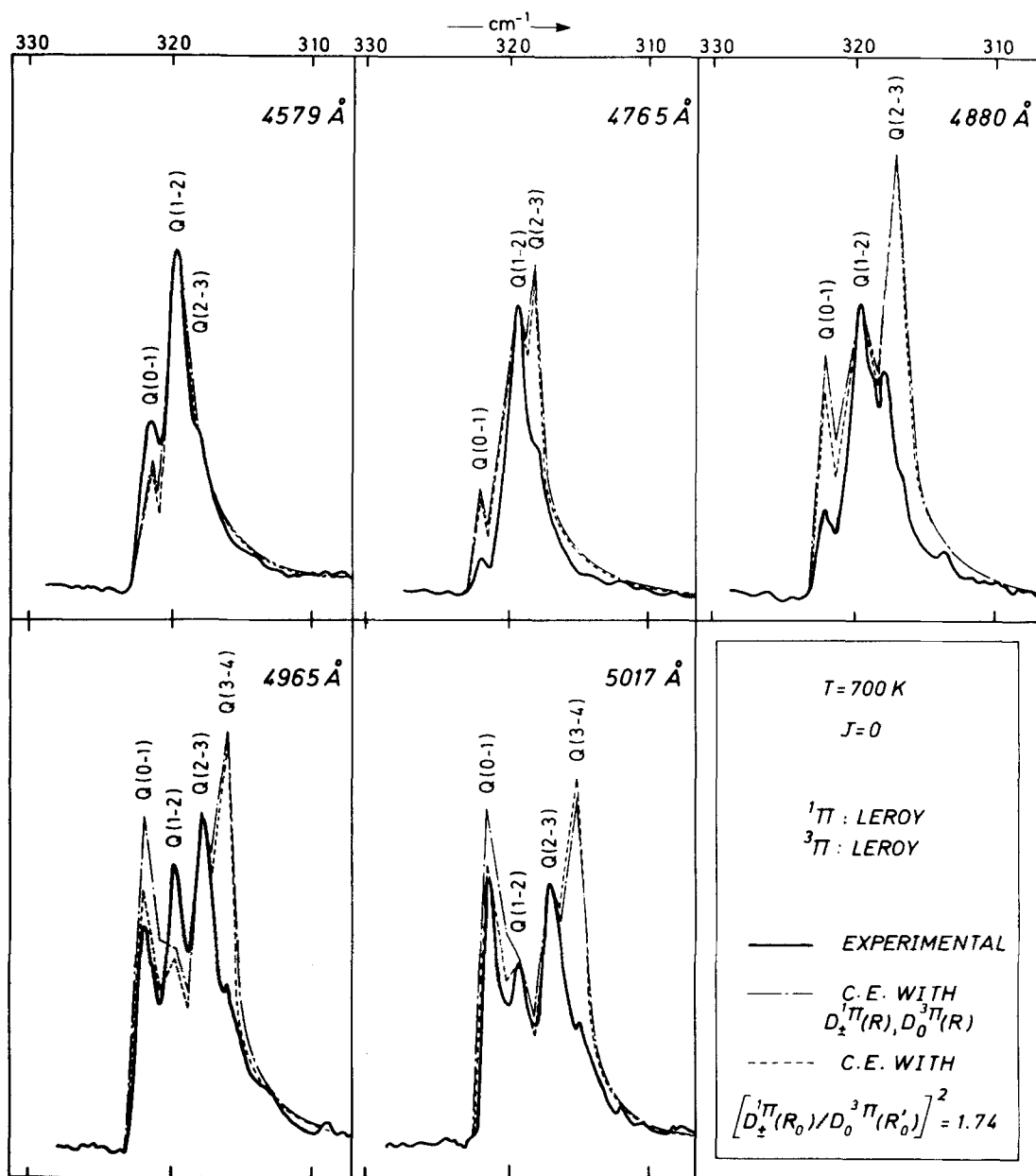


FIG. 3. Experimental and calculated (coupled equations) profiles with Le Roy's potentials<sup>11</sup> with and without  $R$  dependence of the electronic transition moments.

$Q(4-3)$  peak of the semiclassical profile has too low an intensity. This could be traced to  $\Gamma_{43}/\beta^2$  which are respectively  $-0.6357 - 3$  (semiclassical) and  $-0.6912 - 3$  (coupled channel). The replacement of the former number by the latter in the calculation was enough to bring the entire semiclassical profile to agreement with its coupled channel counterpart.

In conjunction with these semiclassical calculations, it is interesting to note that the semiclassical amplitudes depend on the potentials of the excited states only through a definite integral going from  $a_1$  (turning point in the upper potential) to  $R'_c$  (pseudocrossing point for the incident photon energy) or from  $a_1$  to  $R''_c$  (pseudocrossing point for the outgoing photon energy). Table III gives, again for the Coxon potentials, the intervals

which matter in the calculation for each amplitude of each profile. A striking result is that these intervals are very narrow. For instance, the overall range for the 5017 Å is, for the  $^1\Pi$  potential, from 2.4090 to 2.4371 Å, while the overall range for this same potential for the set of the five profiles considered here goes only from 2.3575 to 2.4371 Å. Because of the generally very good agreement between semiclassical and coupled channel results, we are entitled to conclude that although the amplitudes depend in principle on the entire potentials, there is a very narrow effective range. Thus, a profile constitutes in fact a very local test of the potentials.

We may now come back to the effects introduced by the variation with  $R$  of the electronic transition moments.

TABLE II. Comparison of coupled equations (C.E.) and semiclassical (S.C.) scattering amplitudes (in cm) with Coxon's<sup>7b</sup> potentials for Br<sub>2</sub> for the five excitation wavelengths of Baierl and Kiefer.<sup>3</sup>

$n'$	$n''$	$^1\Pi$				$^3\Pi$			
		$\Gamma_{n'n''}$		$\Delta_{n'n''}$		$\Gamma_{n'n''}$		$\Delta_{n'n''}$	
		S.C.	C.E.	S.C.	C.E.	S.C.	C.E.	S.C.	C.E.
$\lambda = 4579 \text{ \AA}$									
1	0	-0.3133-3	-0.3274-3	-0.1924-3	-0.1879-3	0.5344-3	0.5322-3	0.4121-3	0.4252-3
2	1	-0.5537-3	-0.5646-3	0.2293-3	0.2514-3	-0.1686-3	-0.1746-3	0.4049-3	0.4099-3
3	2	0.5160-3	0.4880-4	-0.4934-3	-0.5234-3	-0.1723-3	-0.1841-3	-0.2847-4	-0.3412-4
4	3	0.4107-4	0.4072-4	0.2333-4	0.3291-4	0.1893-4	0.1800-4	0.3910-3	0.4246-3
$\lambda = 4765 \text{ \AA}$									
1	0	-0.1073-3	-0.1120-3	-0.2054-3	-0.2043-3	0.8879-4	0.6422-4	0.8322-3	0.8124-3
2	1	-0.4351-3	-0.4477-3	-0.2031-3	-0.1975-3	-0.6120-4	-0.4625-4	0.8169-5	0.6097-5
3	2	0.5923-3	0.6192-3	-0.2472-3	-0.2700-3	-0.7937-4	-0.7686-4	-0.4690-3	-0.4930-3
4	3	-0.1173-3	-0.1249-3	0.5117-3	0.5624-3	-0.6977-4	-0.6886-4	0.1467-4	0.1613-4
$\lambda = 4880 \text{ \AA}$									
1	0	-0.4124-4	-0.4313-4	-0.1619-3	-0.1605-3	-0.3630-3	-0.3479-3	0.7484-3	0.7552-3
2	1	-0.2424-3	-0.2500-3	-0.2814-3	-0.2807-3	0.2314-3	0.2243-3	0.1415-3	0.1326-3
3	2	0.5789-3	0.6075-3	0.1142-3	0.1109-3	0.2555-3	0.2620-3	-0.3529-3	-0.3722-3
4	3	-0.5490-3	-0.5948-3	0.3849-3	0.4261-3	0.1976-3	0.2154-3	0.1625-3	0.1749-3
$\lambda = 4965 \text{ \AA}$									
1	0	-0.1747-4	-0.1829-4	-0.1298-3	-0.1279-3	-0.5906-3	-0.5797-3	0.5564-3	0.5567-3
2	1	-0.1299-3	-0.1340-3	-0.2639-3	-0.2639-3	0.2475-3	0.2508-3	0.4050-3	0.3994-3
3	2	0.4245-3	0.4461-3	0.2790-3	0.2854-3	0.2525-3	0.2718-3	-0.1013-3	-0.1128-3
4	3	-0.6733-3	-0.7313-3	0.7359-4	0.8750-4	0.1019-3	0.1151-3	0.4120-3	0.4498-3
$\lambda = 5017 \text{ \AA}$									
1	0	-0.3655-5	-0.1011-4	-0.1132-3	-0.1109-3	-0.6714-3	-0.6513-3	0.3974-3	0.4036-3
2	1	-0.8178-4	-0.8443-4	-0.2381-3	-0.2381-3	0.1478-3	0.1550-3	0.5533-3	0.5573-3
3	2	0.3157-3	0.3321-3	0.3199-3	0.3292-3	0.1391-3	0.1521-3	-0.5542-5	-0.1044-4
4	3	-0.6357-3	-0.6912-3	-0.1138-3	-0.1167-3	-0.6912-4	-0.6955-4	0.4655-3	0.5112-3

If in an amplitude such as

$$\lim_{\epsilon \rightarrow 0^+} \int \frac{\langle n'J' | D_{\xi}^e | eE \rangle \langle eE | D_{\xi}^e | n''J'' \rangle}{\bar{E} + i\epsilon - E} dE,$$

the effective range of continuum states is narrow we may expect this amplitude to take the form

$$D_{\xi}^e(R_1) D_{\xi}^e(R_2) \lim_{\epsilon \rightarrow 0^+} \int \frac{\langle n'J' | eE \rangle \langle eE | n''J'' \rangle}{\bar{E} + i\epsilon - E} dE.$$

In fact, the semiclassical expressions [Eqs. (84) and (85) of Paper I] suggest the identification of  $R_1$  with  $R'_c$  and  $R_2$  with  $R''_c$ . In order to check the validity of this assumption, we give in Table II for each of the two potentials the ratios of real and imaginary parts of the amplitudes calculated with and without  $R$ -dependent transition moments ( $r_1$  and  $r_2$  for the  $^1\Pi$  state,  $r'_1$  and  $r'_2$  for the  $^3\Pi$  state). We give also  $p$ , equal to  $D_{\frac{1}{2}}^{1\Pi}(R'_c) \times D_{\frac{1}{2}}^{1\Pi}(R''_c)$  or  $p'$  equal to  $D_{\frac{3}{2}}^{3\Pi}(R'_c) D_{\frac{3}{2}}^{3\Pi}(R''_c)$ . We observe a very close agreement between  $p$  on one hand and  $r_1$  or  $r_2$  on the other and between  $p'$  and  $r'_1$  or  $r'_2$  (except for minor discrepancies which can all be traced to unusually small amplitudes). It is to be noted also that within a given profile all these quantities show only very moderate changes. Thus the introduction of the  $R$  dependence of the electronic transition moments amounts to a multiplication of the amplitudes by  $p$  or  $p'$ . This implies in fact a ratio of the two moments which varies with the exciting wavelength since  $p/p'$  goes from  $\sim 1.71$  for the

4579 Å profile to  $\sim 1.53$  for the 5017 Å profile. It is quite possible to account for the  $R$  dependence of the electronic transition moments without introducing them into the potential matrix of the coupled equations: care should be taken to introduce into the line shape calculation a ratio which takes into account the changes with the incoming photon frequency of the positions of the pseudo-crossing points. We can understand in this way why the  $Q(1-0)$  peak is somewhat enhanced in the 4965 and 5017 Å profiles calculated with  $D_{\frac{1}{2}}^{1\Pi}(R)$  and  $D_{\frac{3}{2}}^{3\Pi}(R)$  since this amounts to reduced effective ratios. Reduction of the ratio increases the  $Q(1-0)$  peak, which is the only peak present in the spectrum produced by the  $^3\Pi$  state.

## VI. PROFILE CALCULATIONS WITH ROTATION

We can observe in Fig. 4 the results of introducing the rotational effects with  $J$  up to 150. The ratio of transition moments is again 1.74 and the temperature 700 K. The only noticeable effect is a slight reduction in the intensity of the  $Q(4-3)$  peak in the profiles with the lower photon frequency. However, this reduction is far from being enough to remove these peaks which never emerge from the background in the experimental spectra. We conclude from this comparison that no drastic changes are brought about by introducing the rotation although some individual intensities may be strongly affected.



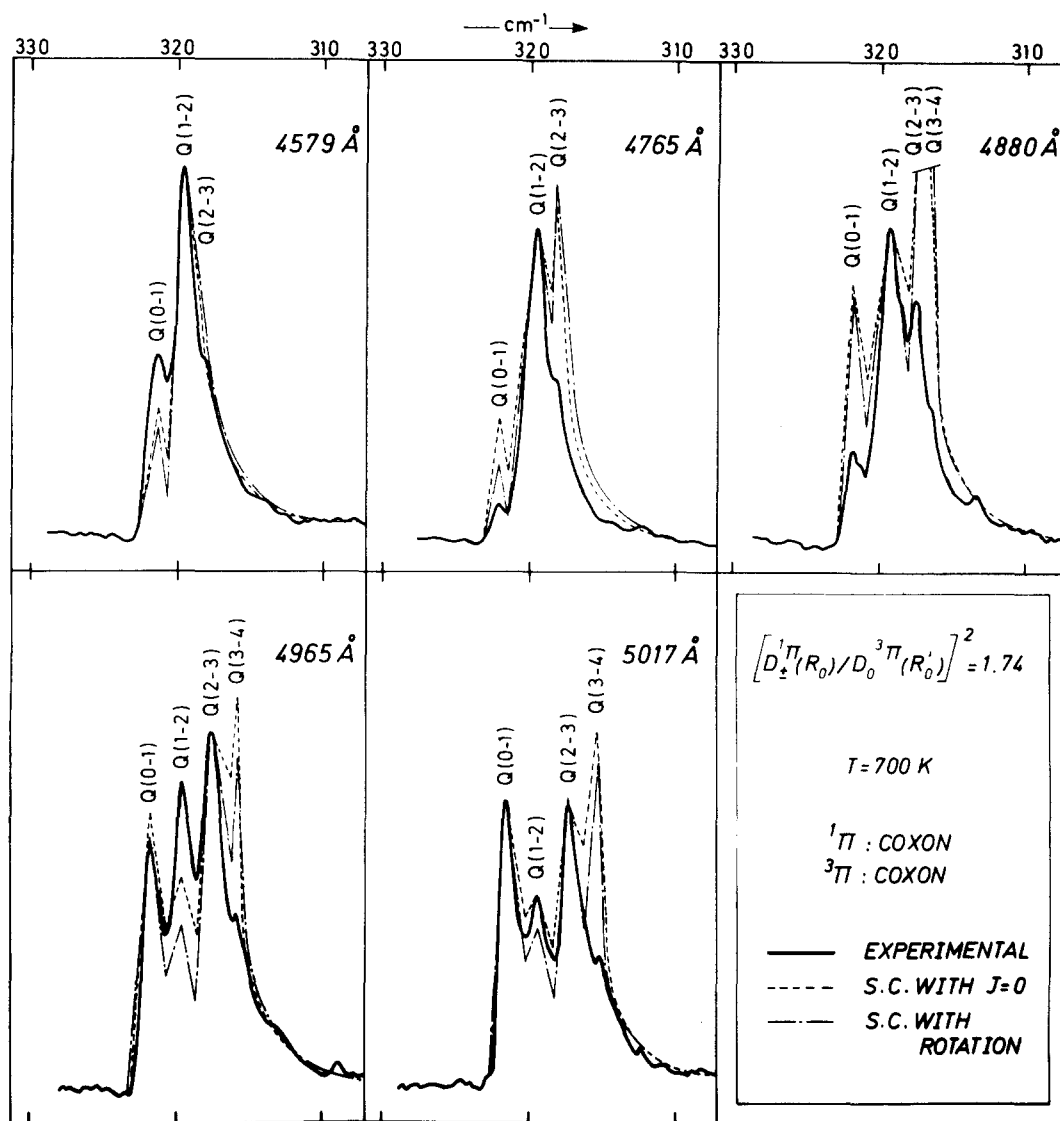


FIG. 4. Experimental and calculated (semiclassically) profiles with Coxon's potentials.<sup>7b</sup> The amplitudes are determined with and without the effect of  $J$ .

It would appear at this point that the next stage in this study should be to look for other potentials which could lead to a better agreement between calculated and experimental profiles. We attempted to make some changes, taking advantage of the fact that in a semiclassical approach each profile requires only local adjustments of the potentials. Although we were led in this way to greatly improved results, the local potentials obtained by this procedure could not be fitted reasonably into single-well behaved potentials for the entire range of internuclear distances that is involved in the calculation of the five profiles.

The examination of the set of profiles obtained with the Coxon's potentials suggests at least a direction for a modification of the potentials. We recall that the 4579 Å profile is rather insensitive to the choice of potentials. The calculated 4765 Å profile looks somewhat like that observed for  $\lambda = 4880$  Å [strong  $Q(2-1)$  and  $Q(3-2)$  peaks]. The calculated 4880 Å has some features in common with the observed 4965 Å [emergence

of a triplet made of  $Q(1-0)$ ,  $Q(2-1)$  and the group  $Q(3-2)$ ,  $Q(4-3)$ ]. The calculated 4965 Å profile presents the triplet characteristic of the observed 5017 Å profile with  $Q(2-1)$  of lower intensity than its two neighbors  $Q(1-0)$  and the combination  $Q(3-2)$ ,  $Q(4-3)$ . It is easy to understand, with the picture of the dressed molecule, that changing the photon frequency together with submitting the excited states potentials to an equal vertical displacement has no effect on the spectra. The correspondence which has been noted above suggests that a local downward displacement of the potentials could improve the profiles. We present in Fig. 5 the best results obtained in such a way with a displacement of  $-400$  cm<sup>-1</sup>, a ratio for squared transition moments equal to 1.8 and a temperature  $T = 600$  K (increasing the ratio of transition moments and lowering the temperature also has favorable effects, but we are somewhat limited in the choice of these parameters). The profiles are calculated again either without or with rotation. There is a considerable improvement in the results, the only serious unsatisfactory feature which re-

TABLE III. Effective ranges for the  $^1\Pi$  and  $^3\Pi$  states of  $\text{Br}_2$  with Coxon's potentials.<sup>7b</sup>  $a_1$  is the turning point in the excited state,  $R_c'$  and  $R_c''$  the radiative crossing points.  $p$  (or  $p'$ ) is the product of the electronic transition moments at  $R_c'$  and  $R_c''$ ;  $r_1$  (or  $r_1'$ ) is the ratio of the real parts of scattering amplitudes with or without  $R$  dependence of transition moments;  $r_2$  (or  $r_2'$ ) the ratio of imaginary parts.

$n'$	$n''$	$^1\Pi$						$^3\Pi$			
		$R_c'$ (Å)	$R_c''$ (Å)	$p$	$r_1$	$r_2$	$R_c'$ (Å)	$R_c''$ (Å)	$p'$	$r_1'$	$r_2'$
	$\lambda=4579 \text{ Å}$			$a_1=2.3523 \text{ Å}$					$a_1=2.2558 \text{ Å}$		
1	0	2.3575	2.3495	0.2478	0.2476	0.2477	2.2684	2.2593	0.1451	0.1454	0.1451
2	1	2.3656	2.3575	0.2465	0.2465	0.2465	2.2774	2.2684	0.1469	0.1476	0.1468
3	2	2.3738	2.3656	0.2453	0.2453	0.2462	2.2865	2.2774	0.1488	0.1585	0.1487
4	3	2.3820	2.3738	0.2440	0.2429	0.2449	2.2957	2.2865	0.1507	0.1517	0.1526
	$\lambda=4765 \text{ Å}$			$a_1=2.3803 \text{ Å}$					$a_1=2.2790 \text{ Å}$		
1	0	2.3797	2.3712	0.2444	0.2443	0.2443	2.2930	2.2836	0.1501	0.1503	0.1507
2	1	2.3883	2.3797	0.2431	0.2433	0.2431	2.3024	2.2930	0.1520	0.1986	0.1526
3	2	2.3969	2.3883	0.2418	0.2414	0.2418	2.3118	2.3024	0.1540	0.1547	0.1545
4	3	2.4057	2.3969	0.2405	0.2403	0.2409	2.3214	2.3118	0.1560	0.1857	0.1564
	$\lambda=4880 \text{ Å}$			$a_1=2.3989 \text{ Å}$					$a_1=2.2937 \text{ Å}$		
1	0	2.3931	2.3844	0.2424	0.2423	0.2423	2.3077	2.2982	0.1531	0.1534	0.1580
2	1	2.4020	2.3931	0.2411	0.2412	0.2410	2.3174	2.3077	0.1551	0.1571	0.1550
3	2	2.4110	2.4020	0.2397	0.2407	0.2397	2.3271	2.3174	0.1571	0.1582	0.1570
4	3	2.4201	2.4110	0.2383	0.2380	0.2384	2.3365	2.3271	0.1591	0.1616	0.1591
	$\lambda=4965 \text{ Å}$			$a_1=2.4135 \text{ Å}$					$a_1=2.3048 \text{ Å}$		
1	0	2.4030	2.3940	0.2409	0.2409	0.2408	2.3184	2.3086	0.1553	0.1557	0.1553
2	1	2.4121	2.4030	0.2395	0.2397	0.2394	2.3282	2.3184	0.1573	0.1580	0.1574
3	2	2.4213	2.4121	0.2382	0.2385	0.2381	2.3378	2.3282	0.1597	0.1631	0.1594
4	3	2.4307	2.4213	0.2368	0.2347	0.2368	2.3474	2.3378	0.1614	0.1625	0.1618
	$\lambda=5017 \text{ Å}$			$a_1=2.4228 \text{ Å}$					$a_1=2.3117 \text{ Å}$		
1	0	2.4090	2.3998	0.2400	0.2400	0.2399	2.3249	2.3150	0.1566	0.1572	0.1566
2	1	2.4182	2.4090	0.2386	0.2388	0.2385	2.3346	2.3249	0.1587	0.1592	0.1589
3	2	2.4276	2.4182	0.2372	0.2375	0.2371	2.3443	2.3346	0.1608	0.2003	0.1610
4	3	2.4371	2.4276	0.2358	0.2373	0.2358	2.3540	2.3443	0.1628	0.1638	0.1620

mains being the too strong  $Q(3-2)$  peak of the 4880 Å profile. Introduction of the rotation does not greatly affect the intensities, although we note that the changes generally go in the right direction (cf. the 4965 and 5017 Å profiles in particular).

## VII. CONCLUSION

The results which have been presented above for the available  $\Delta n = 1$  profiles of  $\text{Br}_2$  are not completely successful. The local downward displacement of  $400 \text{ cm}^{-1}$  which seems to be necessary to remove several unpleasant aspects of the calculated spectra is probably higher than the shift compatible with the uncertainties in the analysis of absorption spectra which can reasonably be estimated to be at most  $200 \text{ cm}^{-1}$ . There might be some other reasons for the difficulties in this analysis.

We believe that a possibility which should be explored in future work is that there might be a nonnegligible contribution to the Raman spectra due to the  $A(^3\Pi_{1u})$  state which is also present in this region. Coxon<sup>12</sup> has estimated that

$$(D_0^{B(^3\Pi_{0u})}/D_0^{A(^3\Pi_{1u})})^2 \approx 28. \quad (15)$$

The situation in a Raman spectrum is somewhat different from that in the absorption spectrum since interference effects bring contributions depending on the product of transition moments to different states. This means that a state may well be contributing very little to absorption while contributing much more to Raman scattering via this interference effect. As a hint that we may have to bring into the calculations this additional state, we may mention the fact that while searching for potentials which would fit both the 4965 and 5017 Å profiles we found it very difficult to reach agreement with the same potentials, although there is a considerable overlapping of the effective ranges. On the other hand, it is precisely in this low frequency region that the  $A(^3\Pi_{1u})$  state is thought to contribute most to the spectra.<sup>12</sup>

Another possibility which deserves examination is the effect of the interstate coupling between the  $^1\Pi$  and  $^3\Pi$  states which is responsible for the predissociation of the bound states of the  $^3\Pi$ .<sup>13</sup> Such a coupling influences Raman scattering when the amplitude is calculated up to third order, with the opening of two new paths: initial state  $\rightarrow ^1\Pi \rightarrow ^3\Pi \rightarrow$  final state or initial state  $\rightarrow ^3\Pi \rightarrow ^1\Pi \rightarrow$  final state. The coupled equations are very

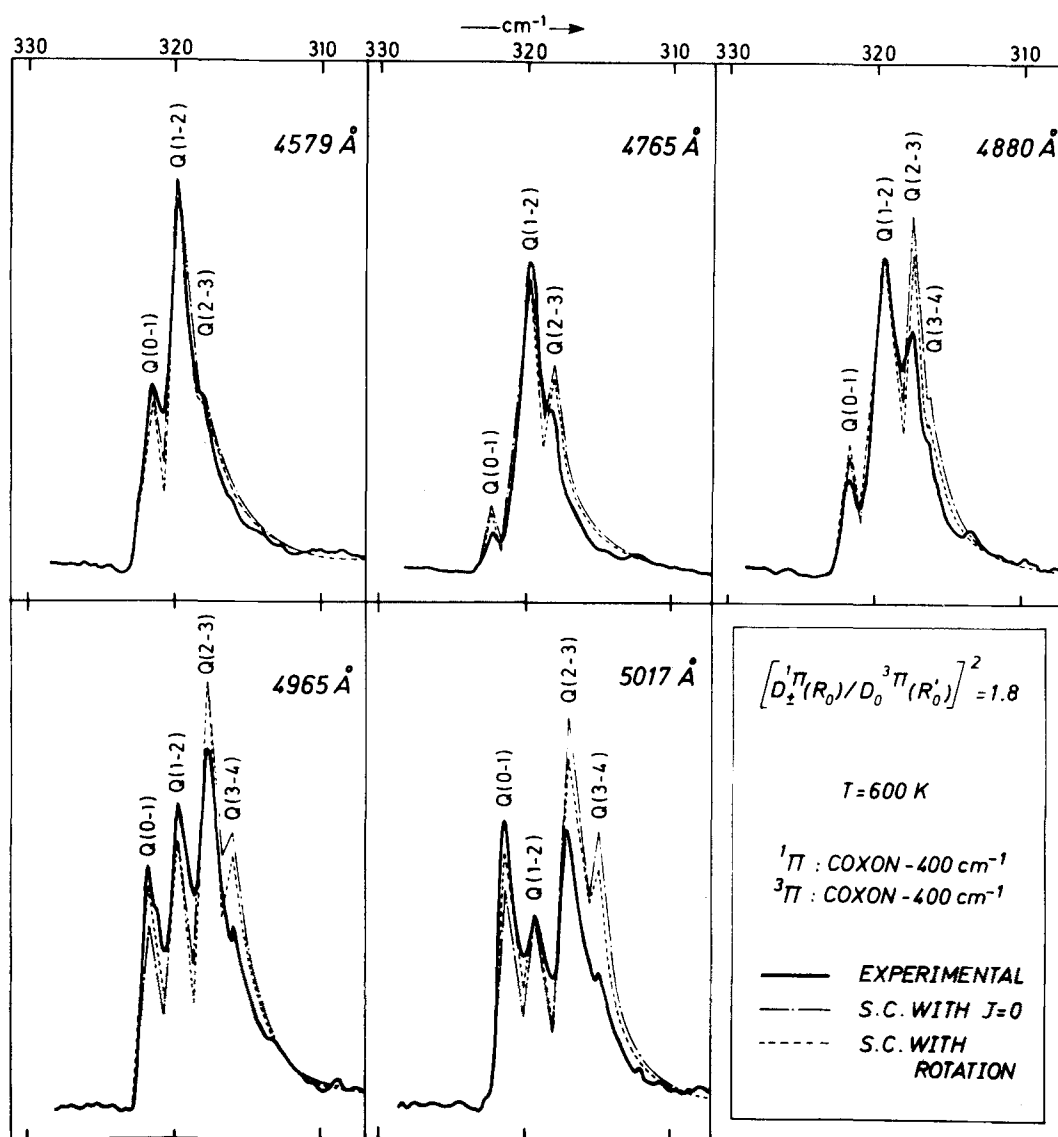


FIG. 5. Experimental and calculated (semiclassically) profiles with displaced Coxon's potentials.<sup>1b</sup> The amplitudes are determined with and without the effect of  $J$ .

convenient to perform the evaluation of such amplitudes. Work is in progress to extend the profile calculations in these two directions.

Beyond these aspects which concern the bromine molecule we believe that on the methodological side the present investigation leads to some conclusions that should be of general interest:

(a) The analysis of a profile corresponding to a given excitation wavelength provides only a very local test of the potentials, as shown by the success of the semiclassical procedure in producing the amplitudes and the fact that this procedure uses only a very narrow part of the potential.

(b) The  $R$  dependence of the electronic transition moments affects the scattering amplitudes only insofar as they change with the pseudocrossings (or radiative crossings) which are involved at a given excitation wavelength.

(c) A relatively minor role is played by the centrifugal energies on profiles which are the superposition of a very large number of lines, although we have observed an unexpectedly large effect on some of the amplitudes.

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