Franck–Condon factors and r-Centroids for the $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ Band System of $^{107,109}Ag_2$: Comparison of the Observed and Calculated Absorption Band Strengths*

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Franck–Condon factors and r-centroids for the $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ band system of $^{107,109}Ag_2$ are computed using Morse and Rydberg–Klein–Rees potentials for both lower and upper electronic states. The differences between the two sets of results are typically in the third decimal place for transitions involving vibrational levels with v' and v'' up to about 15. Somewhat larger deviations appear for higher vibrational levels, but both sets of results follow the same pattern, which is to match well with the relative absorption band strength distribution in our experimental spectrum. The relative absorption band strengths are calculated by assuming that the electronic transition moment has only a weak dependence on the internuclear distance r. Good agreement between our measured and calculated absorption band strength ratios is found, which provides an excellent test of the calculated Franck-Condon factors and relative absorption band strengths. The r-centroid value for the (v' = 0, v'' = 0) band is found to be approximately equal to the average value of r_e' and r_e'', indicating that the potentials of both states are not significantly anharmonic around their minimum regions.

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The A-X band system (4000–5400 Å) is the lowest energy transition in the electronic spectrum of the Ag_2 dimer and results in allowed optical transitions between vibrational levels of the $X^1\Sigma_g^+$ ground state and the first excited $A^1\Sigma_u^+$ state of the molecule. Until 1990, the bands had been investigated by conventional spectroscopic techniques employing different types of King furnaces and discharge tubes as light sources,[1–4] but limited spectral resolution in these experiments permitted only the vibrational analysis of the bands. In 1990–1993, several authors performed rotational analyses of a few highly resolved A–X bands obtained by modern laser spectroscopic techniques and determined very accurate rotational constants for both the electronic states involved in the transition.[5–7] These constants, together with those evaluated in earlier vibrational analyses, offered the opportunity to compute the radiative transition parameters governing the intensity distribution in the vibrational structure of the A–X system, and to compare the predicted absorption band strength distribution with that observed in the experimental spectrum. To our knowledge, no such data have been available until now.

In this Letter, we report the Franck–Condon factors and r-centroids for the A–X bands of the $^{107,109}Ag_2$ isotopomer, which is the most abundant dimer in the gas phase of natural silver. We also present the results of a comparison between our theoretically predicted and experimentally observed relative band strengths in the absorption spectrum.

The relative absorption band strength (measured signal) of the $v' \leftarrow v''$ transition is proportional to the product of three terms:

$$I_{v'v''} \propto N_{v''}\nu_{v'v''}p_{v'v''}, \tag{1}$$

where $N_{v''}$ is the population of the v'' level, $\nu_{v'v''}$ is the wavenumber of the transition, and $p_{v'v''}$ is the relative vibrational transition probability defined as

$$p_{v'v''} \equiv [\langle\psi_{v'}(r)|R_e(r)|\psi_{v''}(r)\rangle]^2, \tag{2}$$

which accounts for the main feature of the vibrational intensity distribution in an electronic transition. Here $\psi_{v'}(r)$ and $\psi_{v''}(r)$ are the wave functions of the rotationless ($J = 0$) vibrational levels in the upper and lower electronic states, respectively, and $R_e(r)$ is the electronic transition moment function, which is generally a function of internuclear distance r. For many band systems, $R_e(r)$ can be well approximated by a constant or a linear function of r, at least in regions where the integrand in Eq. (2) is appreciable. In this case, the r-centroid approximation can be employed,[8–11] and Eq. (2) becomes

$$p_{v'v''} \approx [\langle\psi_{v'}(r)|\psi_{v''}(r)\rangle]^2 R_e^2(\bar{r}_{v'v''}). \tag{3}$$

The first term is the square of overlap integral or Franck–Condon factor (FCF), $q_{v'v''}$, and the function argument in the second term is the weighted mean of the internuclear distance or r-centroid, $\bar{r}_{v'v''}$,for the (v', v'') band:

$$q_{v'v''} \equiv [\langle\psi_{v'}(r)|\psi_{v''}(r)\rangle]^2, \tag{4}$$

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$$\bar{r}_{v'v''} \equiv \frac{\langle \psi_{v'}(r)|r|\psi_{v''}(r)\rangle}{\langle \psi_{v'}(r)|\psi_{v''}(r)\rangle}. \quad (5)$$

The accuracy in the calculation of $q_{v'v''}$ and $\bar{r}_{v'v''}$ depends primarily on the choice of suitable potential energy curves used in the radial Schrödinger equation to solve for the rotationless vibrational wave functions $\psi_{v'}(r)$ and $\psi_{v''}(r)$.

Reasonable agreement between the experimental values of the rotational constants α'_e ($= 2.19 \times 10^{-4}\,\mathrm{cm}^{-1}$) and α''_e ($= 2.08 \times 10^{-4}\,\mathrm{cm}^{-1}$) of Ref. [7] and those calculated using the Pekeris relation[12] with spectroscopic constants from Refs. [1,7] ($\alpha'_e = 2.01 \times 10^{-4}\,\mathrm{cm}^{-1}$ and α''_e ($= 1.95 \times 10^{-4}\,\mathrm{cm}^{-1}$) suggests that the lower part of the potential energies of both states can be well described by a simple Morse function. However, because a number of observed bands result in transitions between fairly high vibronic levels (with v' and v'' above 20), and because the FCFs are very sensitive to the shape of potential curves, we have also applied Rydberg–Klein–Rees (RKR) potentials in our calculations of $\psi_{v'}(r)$ and $\psi_{v''}(r)$.

Table 1 Franck–Condon factors and r-centroids for the $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ band system of ^{107}Ag and ^{109}Ag. For each v'-v'' band, the listed quantities are band-origin wavelengths ($\lambda_{v'v''}$, in μm), Morse-FCFs ($q_{v'v''}$ values computed with Morse potentials), RKR-FCFs ($q_{v'v''}$ values computed with RKR potentials), r-centroids computed with RKR potentials ($\bar{r}_{v'v''}$, in Å). Values of $q_{v'v''} < 0.01$ are marked with an asterisk to indicate possible lower accuracy, and Morse FCFs differing from the corresponding RKR FCF by more than 10% are marked with a dagger.

v'	$v''=0$	1	2	3	4	5	6	7	8	9	10
0	0.4352[a]	0.4389[a]	0.4426	0.4463	0.4500	0.4538	0.4577	0.4616	0.4655	0.4694	0.4734
	1.19E–01	2.68E–01	2.87E–01	1.92E–01	9.07E–02	3.20E–02	8.75E–03*	1.89E–03*	3.31E–04*†	4.69E–05*†	5.44E–06*†
	1.18E–01	2.70E–01	2.89E–01	1.92E–01	8.94E–02	3.09E–02	8.26E–03*	1.74E–03*	2.96E–04*	4.08E–05*	4.61E–06*
	2.5924	2.6247	2.6579	2.6919	2.7268	2.7628	2.7998	2.8381	2.8778	2.9190	2.9620
1	0.4323[a]	0.4359[a]	0.4396	0.4432	0.4470	0.4507	0.4545	0.4583	0.4622	0.4661	0.4700
	2.36E–01	1.51E–01	7.42E–04*	9.27E–02	2.02E–01	1.77E–01	9.41E–02	3.49E–02	9.62E–03*	2.05E–03*	3.43E–04*†
	2.32E–01	1.52E–01	6.93E–04*	9.53E–02	2.06E–01	1.77E–01	9.25E–02	3.35E–02	9.01E–03*	1.87E–03*	3.05E–04*
	2.5664	2.5973	2.6076	2.6659	2.6991	2.7337	2.7695	2.8064	2.8446	2.8843	2.9255
2	0.4295[a]	0.4331	0.4367[a]	0.4403[a]	0.4439	0.4476	0.4514	0.4551	0.4589	0.4628	0.4667
	2.49E–01	4.94E–03*†	1.13E–01	1.03E–01	1.15E–04*†	8.64E–02	1.80E–01	1.51E–01	7.67E–02	2.69E–02	6.93E–03*
	2.45E–01	5.74E–03*	1.12E–01	1.04E–01	6.04E–05*	8.99E–02	1.83E–01	1.51E–01	7.49E–02	2.56E–02	6.45E–03*
	2.5412	2.5650	2.6054	2.6360	2.5742	2.7070	2.7408	2.7763	2.8131	2.8512	2.8908
3	0.4267[a]	0.4302	0.4338[a]	0.4374	0.4410	0.4446	0.4483	0.4520	0.4558	0.4596	0.4634
	1.87E–01	4.31E–02†	1.10E–01	3.03E–03*†	1.15E–01	5.60E–02	6.29E–03*†	1.13E–01	1.70E–01	1.21E–01	5.43E–02
	1.86E–01	3.90E–02	1.11E–01	2.60E–03*	1.16E–01	5.60E–02	7.14E–03*	1.17E–01	1.72E–01	1.20E–01	5.25E–02
	2.5168	2.5503	2.5781	2.6245	2.6441	2.6746	2.7216	2.7483	2.7833	2.8199	2.8579
4	0.4240[a]	0.4275[a]	0.4310	0.4345[a]	0.4381	0.4417	0.4453	0.4490	0.4527	0.4564	0.4602
	1.12E–01	1.27E–01	1.20E–02†	9.39E–02	3.50E–02	3.70E–02	1.05E–01	1.37E–02	3.68E–02	1.43E–01	1.52E–01
	1.13E–01	1.20E–01	1.45E–02	9.16E–02	3.69E–02	3.67E–02	1.07E–01	1.31E–02	3.94E–02	1.47E–01	1.52E–01
	2.4931	2.5245	2.5490	2.5863	2.6141	2.6535	2.6830	2.7103	2.7575	2.7905	2.8267
5	0.4214	0.4248	0.4282	0.4317	0.4352	0.4388	0.4424	0.4460	0.4496	0.4533	0.4571
	5.66E–02	1.49E–01	1.78E–02†	8.02E–02	1.75E–02†	8.79E–02	2.20E–05*†	8.41E–02	6.27E–02	1.84E–03*†	8.73E–02
	5.90E–02	1.44E–01	1.34E–02	8.31E–02	1.51E–02	8.95E–02	4.97E–05*	8.52E–02	6.30E–02	1.32E–03*	9.13E–02
	2.4701	2.5004	2.5356	2.5595	2.5974	2.6231	2.5339	2.6911	2.7218	2.7879	2.7983
6	0.4188	0.4221	0.4255	0.4290	0.4325	0.4360	0.4395	0.4431	0.4467	0.4503	0.4540
	2.53E–02	1.17E–01	8.24E–02†	8.93E–03*†	8.71E–02	4.34E–03*†	7.50E–02	2.83E–02	3.08E–02	9.30E–02	1.30E–02
	2.74E–02	1.17E–01	7.47E–02	1.19E–02	8.46E–02	6.03E–03*	7.39E–02	3.01E–02	3.08E–02	9.45E–02	1.25E–02
	2.4478	2.4773	2.5084	2.5304	2.5677	2.5885	2.6314	2.6586	2.7008	2.7301	2.7570
7	0.4162	0.4195	0.4229	0.4263	0.4297	0.4332	0.4367	0.4402	0.4438	0.4474	0.4510
	1.02E–02	7.23E–02	1.19E–01	1.42E–02†	5.64E–02	3.70E–02†	4.41E–02	2.64E–02	6.81E–02	8.73E–04*	8.17E–02
	1.17E–02	7.52E–02	1.12E–01	8.93E–03*	6.14E–02	3.20E–02	4.81E–02	2.41E–02	7.03E–02	6.91E–04*	8.28E–02
	2.4262	2.4549	2.4848	2.5209	2.5415	2.5769	2.6024	2.6414	2.6679	2.7409	2.7382
8	0.4137	0.4170	0.4203	0.4237	0.4271	0.4305	0.4339	0.4374	0.4409	0.4445	0.4480
	3.82E–03*†	3.76E–02	1.06E–01	6.37E–02†	3.32E–03*†	7.80E–02	1.56E–03*†	7.17E–02	2.69E–04*†	7.41E–02	1.14E–02†
	4.67E–03*	4.13E–02	1.05E–01	5.69E–02	6.86E–03*	7.71E–02	4.28E–04*	7.31E–02	2.55E–05*	7.47E–02	1.28E–02
	2.4053	2.4333	2.4622	2.4930	2.5108	2.5497	2.6185	2.6110	2.8241	2.6762	2.7006
9	0.4112	0.4145	0.4178	0.4211	0.4244	0.4278	0.4312	0.4347	0.4381	0.4416	0.4452
	1.33E–03*†	1.73E–02†	7.26E–02	9.81E–02	1.62E–02†	3.62E–02†	5.29E–02†	1.12E–02†	5.83E–02	1.40E–02†	4.62E–02
	1.77E–03*	2.02E–02	7.55E–02	9.17E–02	9.04E–03*	4.33E–02	4.66E–02	1.56E–02	5.54E–02	1.70E–02	4.49E–02
	2.3852	2.4124	2.4405	2.4698	2.5056	2.5238	2.5582	2.5808	2.6194	2.6433	2.6850
10	0.4088	0.4120	0.4153	0.4186	0.4219	0.4252	0.4286	0.4320	0.4354	0.4388	0.4423
	4.38E–04*†	7.48E–03*†	4.13E–02	9.49E–02	6.01E–02†	3.97E–04*†	6.43E–02	1.50E–02*†	4.26E–02†	2.39E–02†	4.46E–02
	6.43E–04*	9.11E–03*	4.59E–02	9.20E–02	4.92E–02	2.77E–03*	6.67E–02	9.73E–03*	4.80E–02	1.96E–02	4.84E–02
	2.3658	2.3922	2.4195	2.4479	2.4783	2.4878	2.5323	2.5701	2.5912	2.6297	2.6537

[a] Bands observed in our laboratory for this work.

We calculate the Morse-potential FCFs and r-centroids for transitions involving v' and v'' levels up to 20 using a suitably modified Felenbok computer programme[13] and the spectroscopic constants from Refs. [1,7] as input data. Integration is performed between limits 2.2 and 3.0 Å in steps of 0.003 Å. Our computation of RKR parameters is carried out for transitions involving v' and v'' levels up to 30 using

the RKR/FCF computer programmes developed by Espy[11] and the aforementioned constants. Table 1 represents the 11×11 array of FCFs and r-centroids, together with the computed band-origin wavelengths; the full set of results is too large to be presented here, but may be obtained from the authors upon request.

The agreement between RKR and Morse FCFs is good, typically in the third decimal place for transitions involving v' and v'' levels up to about 15. Deviations slightly increase with v'', but both sets of FCFs follow the same pattern: the most prominent FCFs form an open symmetrical Franck–Condon envelope, which is expected for transitions involving electronic states with different equilibrium geometries, as is the case for the X and the A states of$^{107,109}Ag_2$, where$|\Delta r_e|$ is 0.1240 Å and $|\Delta\omega_e|$ is 37.8 cm^{-1}. The vibrational-sum rule is satisfied for the first four v'' and the first three v' progressions. However, for some bands belonging to these progressions, more precisely for the bands ($v' = 0$,$v'' > 6$), (1,2), (1,$v'' > 7$), (2,1), (2,4), (2,9), (2,10), (3,1), (3,3), (3,5) and (3,6), the FCFs are very small, predicting their absence in the experimental spectrum. Only for a few members (typically three)of the ($4 \leq v' \leq 20$, $v'' > 10$) progressions do the FCFs have appreciable values. Their distribution in the (v',v'') array predicts the appearance of sequences with large $v' - v''$ differences.

We first tested the reliability of our calculated FCFs using the previously obtained spectrum by Kleman and Lindkvist.[1] Although these authors did not make intensity measurements, the missing bands in their list serve to identify the transitions of negligible intensity. The data given in Table 1 show reasonable reasonable agreement: weak transitions (missing bands) are correctly predicted by the FCFs to be weak. The existence of relatively long sequences with large $v' - v''$ differences, going up to $\Delta v'' = -12$, is fully consistent with the distribution of prominent FCFs in the (v', v'') scheme with vibrational levels up to 30.

The agreement between experimental and theoretical results can be judged more directly by a comparison between our observed and calculated relative absorption band strengths. For this purpose, we recorded part of the absorption spectrum using a carbon-furnace apparatus and, from densitometer tracings, measured the band-head heights of twelve bands between 4250 and 4410 Å. The spectrum is complicated to some extent by the presence of three isotopomers, with the following expected abundances:[14] $^{107}Ag_2$ (26.85%),$^{107}Ag^{109}Ag$ (49.93%) and $^{109}Ag_2$ (23.21%). Because the band heads of the three species are not resolved under the dispersion used, the measured peaks contain contributions from all three isotopomers. With respect to their abundances, we attribute 50% of each signal to the $^{107}Ag^{109}Ag$ molecule. Table 2 lists the ratios of our calculated relative absorption band strengths (FCFs with the frequency factor ν taken into account) and the ratios of our experimentally determine the band strengths.

Table 2. Absorption band strength ratios for the $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ band system of ^{107}Ag and ^{109}Ag.

Ratio	Observed	Calculated	Error (%)[a]
$I_{0,0}/I_{2,0}$	0.52	0.48	−7.7
$I_{1,0}/I_{2,0}$	0.87	0.94	8.0
$I_{3,0}/I_{2,0}$	0.76	0.76	0
$I_{4,0}/I_{2,0}$	0.44	0.47	6.8
$I_{1,1}/I_{0,1}$	0.55	0.57	3.6
$I_{4,1}/I_{0,1}$	0.45	0.46	2.2
$I_{3,2}/I_{2,2}$	0.95	0.99	5.0
$I_{4,3}/I_{2,3}$	0.90	0.89	−1.1

[a] (Calculated−Observed)/Observed × 100

Despite the considerable uncertainty in our experimental band strength measurements, it is evident from Table 2 that the relative band strength pattern calculated from FCFs matches with the experimental intensity distributions well, and thus offers a good test of the calculated FCFs and relative absorption band strengths. The r-centroid values for the observed bands increase systematically with increasing wavelength in each progression, which is expected for transitions between states with $r'_e > r''_e$. The r-centroid for the A-X (0, 0) band is approximately equal to $(r'_e + r''_e)/2$, which occurs when the potentials of the upper and the lower states are closely harmonic. In conclusion, we believe that our reported FCFs are reliable for most practical applications: calculations of absorption band oscillator strengths, Einstein coefficients (radiative transition probabilities), populations of the initial levels, etc., while our computed r-centroids are useful in determining the r-dependence of the electronic transition moment function over a wide range of r.

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