Franck–Condon factors and observed band strength distribution in the vibrational structure of the Ag$_2$ *D-X* band system

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Abstract: Potential curves for the $X^1\Sigma_g^+$ and $D^1\Sigma_u^+$ states of three diatomic silver isotopomers, ^{107}Ag$_2$, ^{107}Ag^{109}Ag and ^{109}Ag$_2$, were determined from the best available molecular constants by the Rydberg–Klein–Rees method. From these potentials, Franck–Condon factors and band-origin wavenumbers were computed, and the reliability of the obtained values was verified by comparison with the observed band strength distribution and the measured band origin positions in a previously recorded *D-X* spectrum. The ratios of the Franck–Condon factors to those of corresponding isotopic bands were found to be very close to unity, revealing only a very small isotopic effect on the Franck–Condon factors of Ag$_2$ *D-X* bands. The isotopic shifts of the calculated band origins agree well with previously measured displacements of band heads.

Keywords: Franck–Condon factors; band strength distribution; Ag$_2$ *D-X* band system; isotopic effect.

INTRODUCTION

The electronic spectrum of the silver dimer, Ag$_2$, as known to date, consists of six well-developed systems with the red degraded bands between 160–540 nm having a common lower state, $^1\Sigma_g^+$, which is the ground state of the molecule. The systems were identified to belong to: $A^1\Sigma_u^+–X^1\Sigma_g^+$ (400–540 nm), $B^1\prod_u–X^1\Sigma_g^+$ (275–295 nm), $C^1\prod_u–X^1\Sigma_g^+$ (264–271 nm), $D^1\Sigma_u^+–X^1\Sigma_g^+$ (256–261 nm), $E^1\prod_u–X^1\Sigma_g^+$ (247–256 nm) and $H^1\Sigma_u^+–X^1\Sigma_g^+$ (169–173 nm) transitions, and all, with the exception of the *H-X* system, were observed in absorption and partly in emission as early as the 1950s.[1–3] Kleman and Lindkvist[2] gave the most complete data for bands of the *A-X* system, while the work of Ruamps[3] provided a better description of the *B-X*, *C-X*, *D-X* and *E-X* systems. About twenty years

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later, Brown and Ginter[4] re-photographed these bands in absorption and re-corded, for the first time, the *H-X* transition in the vacuum ultraviolet, in addition to the known systems. Due to the limited spectral resolution in the conventional absorption and emission spectroscopy used in their experiments, the authors were able to perform only a vibrational analysis of the bands, which was supported by Srdanov and Pesić based on isotope shift measurements.[5,6] At the beginning of 1990s, several authors analyzed a few highly resolved bands of the *A-X*, *B-X* and *E-X* systems, obtained by new laser spectroscopic techniques, and derived very accurate rotational constants for all states involved in the transitions.[7–9] Some Ag$_2$ band systems were also investigated in matrix environments, in both absorption and emission.[10–16] In all the aforementioned studies, the attention was focused on the analysis of the bands to yield accurate molecular constants and correct assignment of the involved electronic states. However, information on the transition probability parameters for these bands, at least the Franck–Condon factors (FCFs), which may be the governing parameters for the determination of band strength distributions in the vibrational structure of band systems, is scarce. The only existing sets of FCFs for Ag$_2$ bands from the early work were those for the *B-X* and *C-X* bands reported by Vujisić and Pešić.[17] The authors performed FCF calculations using Morse potential energy functions in a formalism developed by Fraser and Jerman[18,19] and molecular constants were obtained from their analysis of the spectrum;[5,20] these were later corrected by Beutel *et al.*[9]

Due to the important role of FCFs and related quantities for the prediction of vibrational band strength distributions in molecular band systems and for an explanation of the experimentally observed intensity pattern, recently an evaluation of transition probability parameters for all band systems of diatomic silver were undertaken. It was hoped that the obtained data would be useful for both experimentalists and theoreticians in future research on the Ag$_2$ spectrum, which is of interest in many areas, such as studies of small silver clusters, catalysis and surface science.

In the first paper of this series, a large set of FCFs and *r*-centroids for the *E-X* bands based on Morse and Rydberg–Klein–Rees (RKR) potentials were reported, and it was shown that both sets of data agreed fairly well for transitions involving low vibrational levels with ν' and ν'' up to 6, while both sets followed the same intensity pattern.[21] In the following papers, all relevant transition probability parameters for the *A-X* bands were calculated, including FCFs, *r*-centroids, electronic transition moment function (ETMF), Einstein coefficients and absorption band oscillator strengths, and the results of a comparison of theoretical and experimental data.[22,23] The last study involved the experimental and theoretical study of absorption band strengths in the *B-X* system of Ag$_2$ isotopomers.[24]

In the present paper, for the first time, the FCFs for the rather weak *D-X* bands appearing in the transition between the vibronic levels of the lower $X^1\Sigma_g^+$

and the upper $D^1\Sigma_u^+$ states are reported. FCF computation was performed using RKR potential energy curves separately for three diatomic silver isotopomers, $^{107}Ag_2$, $^{107}Ag^{109}Ag$ and $^{109}Ag_2$, which are always present in the gas-phase spectrum of diatomic natural silver. The aim was to analyze the band strength distribution in the experimental spectrum using computed FCFs, and also to see whether isotopic substitution causes a shift in the values of FCFs of isotopic Ag_2 molecules,[25,26] which is of interest in intensity analysis of unresolved isotopic bands and in the determination of the abundances of isotopic molecules present using intensity measurements of resolved isotopic bands.

METHOD OF COMPUTATION

The theoretical background for the present computation can be found in previous papers.[21-23] Briefly, neglecting the effect of rotational–vibrational interaction and assuming a constant ETMF over the range of internuclear distances encountered in the detected transitions (*i.e.*, the *r*-centroid approximation), the measured band strength signal, $I_{v'v''}$, in the absorption electronic spectrum of the diatomic molecule is given by:[27]

$$I_{v'v''} = DN_{v''}\nu_{v'v''}R_e^2(\int \Psi_{v'}\Psi_{v''}dr)^2 \tag{1}$$

where D is a constant, $N_{v''}$ is the population in the lower vibronic state, $\nu_{v'v''}$ is the frequency of the $v'' \rightarrow v'$ transition, R_e is the average ETMF, which is conventionally used as an approximation in the cases where the function varies sufficiently slowly with internuclear distance, and $(\int \Psi_{v'}\Psi_{v''}dr)^2$ is the square of the overlap integral or FCF, $q_{v'v''}$, associated with the $v' \rightarrow v'$ transition. The wavefunctions $\Psi_{v'}$ and $\Psi_{v''}$ are those for the rotationless ($J = 0$) vibrational states.

The computational accuracy of the FCFs depends primarily on the choice of the potential energy functions. Usually, Morse potential functions and Morse wavefunctions can be taken as a fairly satisfactory approximation of the realistic wavefunctions, especially for low vibrational levels. However, since the recorded *D-X* system includes transitions between relatively high vibrational levels with $v' = 14$ and $v'' = 17$ (in the *X* state these levels cover about 22 % of the full potential and about 37 % in the *D* state), RKR potential curves were used for both the *X* and *D* states (Fig. 1) in the radial Schrödinger Equation to solve for $\Psi_{v'}$ and $\Psi_{v''}$ in order to obtain reliable FCF values.

The molecular constants required for the $^{107}Ag^{109}Ag$ calculation are listed in Table I together with the constants for the less abundant isotopomers, $^{107}Ag_2$ and $^{109}Ag_2$, which were derived from the constants of $^{107}Ag^{109}Ag$ using isotope relations:[27]

$$\omega_e^i = \omega_e(\mu/\mu^i)^{1/2}; \quad \omega_e^ix_e^i = \omega_ex_e(\mu/\mu^i); \quad \omega_e^iy_e^i = \omega_ey_e(\mu/\mu^i)^{3/2} \tag{2}$$

$$B_e^i = B_e(\mu/\mu^i); \quad \alpha_e^i = \alpha_e(\mu/\mu^i)^{3/2} \tag{3}$$

where μ is the reduced mass of $^{107}Ag^{109}Ag$ and μ^i is the reduced mass of the less abundant molecules.

The calculation of the RKR potential-FCFs was performed for transitions involving v' and v'' levels up to 21 using the RKR/FCF computer program developed by Espy.[28]

RESULTS AND DISCUSSION

Portions of the 15×21 arrays of the calculated FCFs for all three diatomic silver isotopomers together with computed band-origin wavenumbers of the corres-

ponding bands are contained in Table I (Supplementary material). The FCFs for the transitions v' (from 11 to 21) $\rightarrow v'$ (from 0 to 6) are negligibly small and they are not presented in Table I, nor are those for the transitions $v'' > 15 \rightarrow v'$ (from 0 to 21).
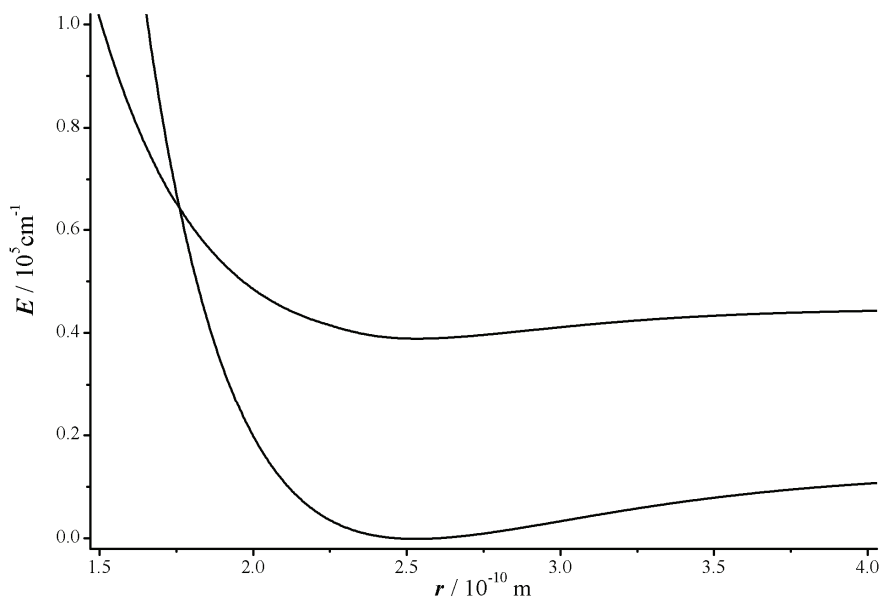

Fig. 1. RKR Potential energy curves for the *X* (lower curve) and *D* (upper curve) states of the ^{107,109}Ag$_2$ molecule.

TABLE I. Molecular constants (cm^{-1}) of the Ag$_2$ $X^1\Sigma g^+$ and $D^1\Sigma u^+$ states used in the RKR computations (The constants for ^{107}Ag$_2$ and ^{109}Ag$_2$ were calculated from the isotopic relations (2) and (3); μ (^{107}Ag^{109}Ag) = 53.94783 amu; μ (^{107}Ag2) = 53.45255 amu; μ (^{109}Ag2) = 54.452378 amu)

Constant	$X^1\Sigma_g^+$			$D^1\Sigma_u^+$		
	^{107}Ag^{109}Ag	^{107}Ag$_2$	^{109}Ag$_2$	^{107}Ag^{109}Ag	^{107}Ag$_2$	^{109}Ag$_2$
T_e	−96.039[a]	−96.039	−96.039	38918.4	38918.4	38918.4
ω_e	192.40[b]	193.289	191.506	168.2[c]	168.977	167.419
$\omega_e x_e$	0.643[b]	0.649	0.637	1.20[c]	1.210	1.189
$\omega_e y_e$	0.0003[b]	0.000304	0.000296			
D_e	13403.1	13404.9	13404.0	5894.3	5899.0	5893.6
B_e	0.04881[d]	0.04926	0.04836	0.04865[d]	0.04910	0.04820
$\alpha_e \times 10^{-4}$	2.08[c]	2.11	2.05	2.82[c]	2.86	2.78

[a]Re-adjusted T_e such that T_0 ($v' = 0$) = 0 for $v_0(0,0)$ = 39002.2 cm^{-1} of Brown and Ginter; [b]Ref. 2; [c]Ref. 3; [d]Ref. 9

A close survey of Table I reveals that the prominent FCFs form a narrow Franck–Condon envelope with a concentration of the highest values on the dia-

gonal axis of the matrix, which is typical for transitions between electronic states having a similar equilibrium distance r_e (see B_e for both states given in Table I).

The distribution of the FCF values in the v',v'' scheme indicates the appearance of a $\Delta v = 0$ sequence as the strongest one in the system, followed by the much weaker bands of a few other sequences with low $\Delta v = v' - v''$ values. Very small FCFs for the transitions $v' > v' + 1 \rightarrow v'$ (from 0 to 1), $v' > v' + 2 \rightarrow v'$ (from 2 to 3), $v' > v' + 3 \rightarrow v'$ (from 4 to 5) and $v' > v' + 4 \rightarrow v'$ (from 6 to 7) suggest the absence a few first members in the $\Delta v = -1, -2, -3$ and -4 sequences.

To verify the reliability of the calculated FCFs, data previously reported by Srdanov and Pešić[5] on the *D-X* system was used. They listed band heads for 41 bands of the $^{107}Ag^{109}Ag$ isotopomer belonging to five sequences ($\Delta v = 0, -1, -2, -3$ and -4), which are included in the v', v'' scheme shown in Fig. 2. The bands of the $\Delta v = 0$ sequence were visually estimated by the authors as the most intense in the system, while all other bands were estimated to be much weaker.
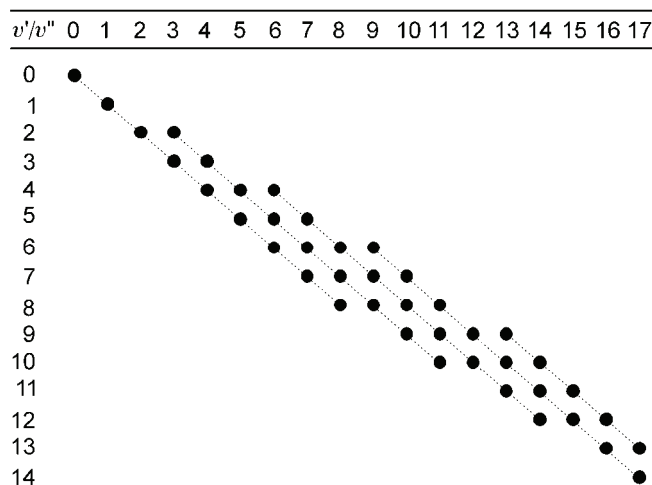

Fig. 2. Recorded *D-X* bands of $^{107}Ag^{109}Ag$.

As can be seen from Fig. 2, the distribution of the bands in the v',v'' scheme is generally consistent with that of the prominent FCFs in Table I. The recorded bands form a narrow envelope with the first two members missing in the $\Delta v = -1$ sequence, the first four missing in the $\Delta v = -2$ sequence, the first six and the first eight members missing in the $\Delta v = -3$ and $\Delta v = -4$ sequences, respectively. The absence of these features was predicted by the computed FCFs.

An attempt was made to judge more directly the agreement between experimental and theoretical results by comparing the ratios of the measured relative bands strengths of the bands having a common lower vibrational level with those theoretically computed for the same bands using the computed FCFs and quoted

wavenumbers. For this purpose, a portion of the *D-X* system containing the bands of the $\Delta v = 0$ and $\Delta v = -1$ sequences was recorded in absorption as described elsewhere.[22] The microphotometer tracing of the recorded bands is shown in Fig. 3.
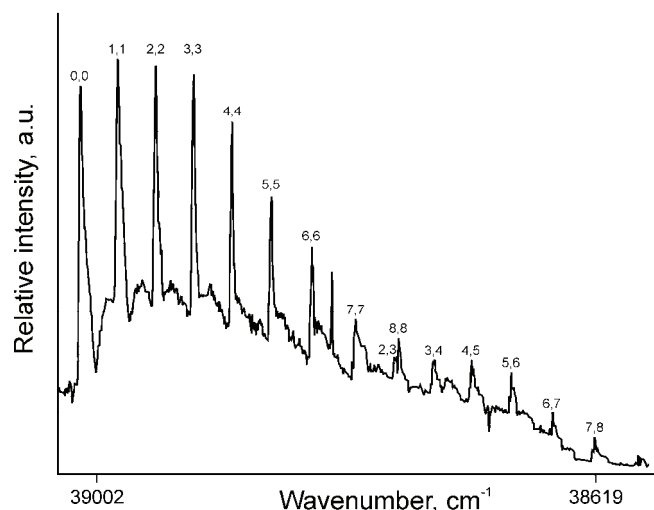

Fig. 3. Microphotometer trace of the recorded Ag$_2$ *D-X* bands of the $\Delta v = 0$ and -1 sequences.

However, due to the very low band strengths of the $\Delta v = -1$ sequence bands and, consequently, very low accuracy of the measurement of their intensity, the attempt was not successful. Therefore, as an additional check on the accuracy of the RKR calculations, a comparison of the band origin wavenumbers obtained in this study were compared with those measured by Brown and Ginter[4] at the positions of the intensity minima clearly seen in several bands of the $\Delta v = 0$ sequence (these wavenumbers are given in the note of Table I).

In addition, the isotopic shifts calculated in the present work were compared with those measured by Srdanov and Pešić,[5] in whose spectrum the heads of 19 bands belonging to three diatomic silver isotopomers, ^{107}Ag$_2$, ^{107}Ag^{109}Ag and ^{109}Ag$_2$, were resolved.[5] In both cases, agreement within experimental error was found. The isotope shifts of the calculated band origins, $\Delta \dot{v}_0 = v_0(^{107}Ag_2 - v_0(^{107}$Ag^{109}Ag$)$ and $\Delta \ddot{v}_0 = v_0(^{109}Ag_2 - v_0(^{107}$Ag^{109}Ag$)$, as well as the isotopic displacements of the band heads, $\Delta \dot{v}_h = v_h(^{107}Ag_2 - v_h(^{107}$Ag^{109}Ag$)$ and $\Delta \ddot{v}_h = v_h(^{109}Ag_2 - v_h(^{107}$Ag^{109}Ag$)$ measured by Srdanov and Pešić, are presented in Table II.

Finally, it is worthwhile to point out the very small isotopic effect seen in the FCFs of the *D-X* bands of Ag$_2$ isotopomers. As follows from Table I, the ratios $q(^{107}$Ag$_2)/q(^{107}$Ag^{109}Ag$)$ and $q(^{109}$Ag$_2)/q(^{107}$Ag^{109}Ag$)$ are very close to unity for all the observed bands, with discrepancies at the third decimal place. This is of interest to know for intensity analysis of unresolved isotopic bands, since, in

such cases, the measured strength signal contains contributors from all isotope-mers present, as well as for the study of abundances of the isotope species present based on intensity measurements of isotopic resolved bands.

TABLE II. Isotope shifts $\Delta\nu_0^i$ and $\Delta\nu_h^i$ in cm^{-1} for the resolved bands of the Ag$_2$ D-X system ν_0, $\nu_0^{i(1)}$ and $\nu_0^{i(2)}$ – calculated band-origin wavenumbers of ^{107}Ag^{109}Ag, ^{107}Ag$_2$ and ^{109}Ag$_2$, respectively; ν_h, $\nu_h^{i(1)}$ and $\nu_h^{i(2)}$ – measured band-head wavenumbers of ^{107}Ag^{109}Ag, ^{107}Ag$_2$ and ^{109}Ag$_2$, respectively)

ν',ν''	$\Delta\nu_0^i = \nu_0^{i(1)} - \nu_0$	$\Delta\nu_h^i = \nu_h^{i(1)} - \nu_h$	$\Delta\nu_0^i = \nu_0^{i(2)} - \nu_0$	$\Delta\nu_h^i = \nu_h^{i(2)} - \nu_h$
5,5	–0.75	–0.8	+0.77	+0.8
6,6	–0.90	–1.0	+0.96	+1.0
7,7	–1.08	–1.2	+1.13	+1.2
8,8	–1.25	–1.4	+1.32	+1.4
3,4	–1.29	–1.3	+1.30	+1.3
4,5	–1.42	–1.5	+1.44	+1.4
5,6	–1.56	–1.6	+1.61	+1.6
6,7	–1.71	–1.8	+1.76	+1.8
7,8	–1.87	–2.0	+1.93	+1.8
8,9	–2.04	–2.2	+2.11	+2.1
9,10	–2.22	–2.4	+2.30	+2.4
4,6	–2.23	–2.3	+2.28	+2.2
5,7	–2.37	–2.4	+2.41	+2.4
6,8	–2.51	–2.6	+2.56	+2.8
7,9	–2.65	–2.7	+2.71	+2.8
8,10	–2.81	–2.9	+2.89	+3.0
9,11	–2.97	–3.1	+3.07	+3.2
10,12	–3.15	–3.3	+3.26	+3.4
11,13	–3.33	–3.6	+3.46	+3.6

CONCLUSIONS

In this paper, FCFs for the *D-X* bands of three diatomic silver isotopomers were derived for the first time using the RKR approach. The reliability of the obtained values was verified by comparison of the predicted band strength distribution based on the calculated FCFs and band-origin wavenumbers with those observed in the experimental *D-X* spectrum.

Comparison of the isotopic shifts of the calculated band origins with experimentally measured band heads in a previously recorded *D-X* spectrum further supports the accuracy of the present RKR-based calculations. The isotope effect on Ag$_2$ *D-X* FCFs was also examined and found to be negligible.

SUPPLEMENTARY MATERIAL

Band-origin wavenumbers in cm^{-1} and FCFs for the $D^1\Sigma_u^+$–$X^1\Sigma_g^+$ bands of ^{107}Ag$_2$, ^{107}Ag^{109}Ag and ^{109}Ag$_2$ (Table I) can be found in the electronic version of the paper as Supplementary material (http://www.shd.org.rs/JSCS/), from the office of the Serbian Chemical Society (JSCS@shd.org.rs) or from the corresponding author upon request.

И З В О Д

ФРАНК-КОНДОНОВИ ФАКТОРИ И ЗАПАЖЕНА РАСПОДЕЛА ЈАЧИНЕ ТРАКА У ВИБРАЦИОНОЈ СТРУКТУРИ Ag_2 *D-X* ТРАКАСТОГ СИСТЕМА

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Користећи најбоље расположиве спектроскопске константе за основно $X^1\Sigma_g^+$ и побуђено $D^1\Sigma_u^+$ стање Ag_2 молекула израчунате су Ридберг–Клајн–Рисове (РКР) потенцијалне криве за оба електронска стања, на којима је засновано израчунавање Франк–Кондонових (ФК) фактора и положаја почетака *D-X* трака. Поменути параметри израчунати су за три изотопна двоатомска молекула, $^{107}Ag_2$, $^{107}Ag^{109}Ag$ и $^{109}Ag_2$, увек присутна у парној фази природног сребра на високим температурама, који је смеша два изотопа: ^{107}Ag (≈51,5 %) и ^{109}Ag (≈48,5 %). Добијене вредности упоређене су са расподелом релативних интензитета трака у експерименталном спектру. Утврђено је да појава интензивних *D-X* трака $\Delta v = 0$ секвенције и много слабијих трака секвенција Δv од 1 до 4, као и њихови релативни интензитети следе предвиђену расподелу интензитета на основу ФК фактора и фреквенција прелаза. Слагање изотопских помераја израчунатих почетака трака изотопних молекула и помераја раније мерених чела трака додатно су потврдили исправност наших РКР-израчунавања. Односи ФК фактора мање обилних изотопних молекула, $^{107}Ag_2$ и $^{109}Ag_2$, и ФК фактора обилнијег изотопа, $^{107}Ag^{109}Ag$, врло блиских јединици, указали су да изотопска замена има занемарљиво мали ефекат на вредности ФК фактора Ag_2 *D-X* трака.

(Примљено 8. јуна 2009, ревидирано 1. фебруара 2010)

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