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Molecular parameters for the gas phase molecules SbO and SbP

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Abstract: Franck–Condon factors and *r*-centroids, which are very closely related to relative vibrational transition probabilities, were evaluated by the numerical integration procedure for the bands of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$, $C^2\mathit{\Sigma} - X^2\Pi_{3/2}$ and $D^2\Pi - X^2\Pi$ systems of the isotopic SbO molecule and for the $B^1\Pi - X^1\Sigma^+$ system of the isotopic SbP molecule, using a suitable potential.

Keywords: Franck–Condon factors; *r*-centroids and isotopic molecule SbO and SbP molecules.

INTRODUCTION

Franck–Condon (F–C) factors are important parameters for every molecular band system, since they enter into the calculation of the relative band intensity, which is a significant source of information in quantitative spectroscopy, high-temperature chemistry, astrochemistry and cometary spectra. They are also important for the determination of the molecular structure, population of the vibrational levels in the upper electronic state involved in a transition, radiative lifetime, vibrational temperature and kinetics of energy transfer in stellar and other astrophysical atmospheres containing molecular species. On the other hand, knowledge of *r*-centroids has been found to be very useful in the discussion of the variation of the electronic transition moment with internuclear separation and in other molecular properties. Variation of *r*-centroids with band wavelengths (or wavenumbers) provides a useful bridge between experimental measurements, which are often expressed as a function of wavelength, and theoretical studies, which are often made in terms of internuclear separation.[1]

Suresh Kumar *et al.*[2] reported that the SbO molecule is likely to be present in the atmosphere of K-type stars and in interstellar space. Spectra of the radiation from astronomical sources show many bands which are attributed to diatomic molecules. A number of lighter as well as heavier diatomic molecules have been detected in stellar spectra, the Earth's atmosphere, planets and in interstellar

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sources. Dealing with 300 diatomic molecules of known or of possible astrophysical interest, Sauval and Tatum[3] also reported polynomial expressions of partition functions and equilibrium constants of the SbH, SbO, SbF and SbP molecules. Based on estimates of the abundances of Sb, the phosphate of antimony is expected to be present in stars. Estimates of the relative abundances of these metallic species are of importance for the understanding of the evolutionary phases of the observed stars and are also essential inputs in the modeling of the stellar atmospheres of late type stars. Their relative abundances in the interstellar medium give estimates of stellar activity, such as supernovae, in the observed region.

To the best of our knowledge, there has been no reports on Franck–Condon factors and r-centroids for the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ system of ^{123}SbO, the $C^2\Sigma - X^2\Pi_{3/2}$ and $D^2\Pi - X^2\Pi$ systems of ^{121}SbO and the $B^1\Pi - X^1\Sigma^+$ system of ^{123}SbO and ^{121}SbP molecules in the literature. Therefore, reliable values of the Franck–Condon factors and *r*-centroids for the above band systems of isotopic SbO and SbP molecules have been computed by a numerical integration procedure, using the suitable potential.

FRANCK–CONDON FACTORS AND *r*-CENTROIDS

Mathematically, one can write for the intensity $I_{v'v''}$ of a molecular band for an electronic transition in emission ($v' \to v''$) as (Straughan and Walker[4]):

$$I_{v'v''} = DN_{v'}E^4_{v'v''}R^2_e(\bar{r}_{v'v''})q_{v'v''} \tag{1}$$

where D is a constant, partly depending on the geometry of the apparatus; $N_{v'}$ denotes the number of molecules in the vibrational level v' of the upper electronic state, determined by the Boltzmann law; $E_{v'v''}$ the energy quantum; $q_{v'v''}$ the Franck–Condon factor; $\bar{r}_{v'v''}$ the *r*-centroid and R_e the electronic transition moment.

The intensities of bands in emission of diatomic molecular are controlled by the value of the Franck–Condon factor, which is the square of the overlap integral between the excited state wave function and the ground state wave function.

$$q_{v'v''} = \left| \langle \Psi_{v'} \mid \Psi_{v''} \rangle \right|^2 \tag{2}$$

where $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wave functions for the upper and lower states, respectively, between which the transition occurs. The *r*-centroid is a unique value of the internuclear separation, which may be associated with the $v' - v''$ band and defined as:

$$\bar{r}_{v'v''} = \frac{\langle \Psi_{v'} \mid r \mid \Psi_{v''} \rangle}{\langle \Psi_{v'} \mid \Psi_{v''} \rangle} \tag{3}$$

For a proper understanding of the intensity distribution in the band systems of molecules, it is necessary to choose a suitable potential. The potential energy curves for the appropriate electronic states of SbO, ^{123}SbP and ^{121}SbP have been constructed using the Morse[5] function and also by the Rydberg–Klein–Rees (RKR) procedure as modified by Vanderslice *et al.*[6,7] It was found that the Morse function represents the potential for the states of SbO, ^{123}SbP and ^{121}SbP quite adequately, since the experimental (RKR) curves are coincident with the Morse ones. The Morse wave functions were calculated at intervals of 0.01 Å for the range of r, respectively, from 1.66 to 2.22 Å, from 1.67 to 2.47 Å, from 1.70 to 2.27 Å, from 2.00 to 2.54 Å and from 2.00 to 2.54 Å for every observed vibrational level of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ system of ^{123}SbO, the $C^2\Sigma - X^2\Pi_{3/2}$ and $D^2\Pi - X^2\Pi$ systems of the ^{121}SbO molecule and the $B^1\Pi - X^1\Sigma^+$ systems of the isotopic ^{123}SbP and ^{123}SbP molecules. The computation of the Franck–Condon factor was made by the Bates[8] method of numerical integration as per the detailed procedure provided by Partal Urena *et al.*[9] Integrals in the Eqs. (2) and (3) for the F–C factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) were computed numerically and the results are presented, respectively, in Tables I, II and III for the $A^2\Pi_{3/2}$ — $X^2\Pi_{3/2}$, $C^2\Sigma - X^2\Pi_{3/2}$ and $D^2\Pi - X^2\Pi$ systems of SbO and in Tables IV and V for the $B^1\Pi - X^1\Sigma^+$ system of the ^{123}SbP and ^{121}SbP molecules. The wavelengths ($\lambda_{v'v''}$) data[10–13] for the band systems of SbO, ^{123}SbP and ^{121}SbP molecules are also included in Tables I–V. The molecular constants used in the present study were collected from the compilation of Huber and Herzberg[14] and they are entered in Table VI.

TABLE I. Franck–Condon factors, r-centroids and wavelengths of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ system of ^{123}SbO

		$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$
$v' = 0$	$q_{v'v''}$	0.002	0.014	0.050	0.112	0.176
	$\bar{r}_{v'v''}$ / Å	1.923	1.943	1.964	1.985	2.007
	$\lambda_{v'v''}$ / Å	–	–	5952.52	6245.33	6564.71
$v' = 1$	$q_{v'v''}$	0.010	0.053	0.119	0.142	0.081
	$\bar{r}_{v'v''}$ / Å	1.909	1.929	1.949	1.969	1.989
	$\lambda_{v'v''}$ / Å	–	5506.45	5758.92	6032.54	–
$v' = 2$	$q_{v'v''}$	0.028	0.099	0.124	0.049	0
	$\bar{r}_{v'v''}$ / Å	1.895	1.914	1.934	1.952	–
	$\lambda_{v'v''}$ / Å	–	5341.82	5579.10	–	–

RESULTS AND DISCUSSION

In the case of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ system of the ^{123}SbO and $C^2\Sigma - X^2\Pi_{3/2}$ systems of the ^{121}SbO molecule, the F–C factors indicate that (0,3), (0,4), (1,2), (1,3) and (2,2), and (0,2), (0,3), (0,4), (1,1), (1,2), (2,0), (2,1), (3,0), (4,0), (5,0) and (6,0) bands are intense (F–C factor > 0.1). For the $D^2\Pi - X^2\Pi$ system, the F–C factors indicate that all the bands are less intense. Since $r_e' > r_e''$, the r-centroids values increase with increasing wavelength, which is expected in the red degraded band system.

TABLE II. Franck–Condon factors, *r*-centroids and wavelengths of the C$^2\Sigma$– X$^2\Pi_{3/2}$ system of 121SbO

		$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$
$v' = 0$	$q_{v'v''}$	0.015	0.070	0.157	0.221	0.220
	$\bar{r}_{v'v''}$ / Å	1.907	1.931	1.956	1.981	2.007
	$\lambda_{v'v''}$ / Å	3581.71	3688.30	–	–	–
$v' = 1$	$q_{v'v''}$	0.053	0.149	0.152	0.051	0
	$\bar{r}_{v'v''}$ / Å	1.890	1.914	1.937	1.961	
	$\lambda_{v'v''}$ / Å	3511.56	3613.89	–	–	
$v' = 2$	$q_{v'v''}$	0.104	0.148	0.033	0.016	0.102
	$\bar{r}_{v'v''}$ / Å	1.874	1.897	1.918	1.949	1.971
	$\lambda_{v'v''}$ / Å	3444.64	–	–	–	–
$v' = 3$	$q_{v'v''}$	0.143	0.079	0.004	0.089	0.045
	$\bar{r}_{v'v''}$ / Å	1.858	1.880	1.911	1.928	1.950
$v' = 4$	$q_{v'v''}$	0.158	0.016	0.056	0.059	0.003
	$\bar{r}_{v'v''}$ / Å	1.843	1.863	1.889	1.910	1.946
$v' = 5$	$q_{v'v''}$	0.148	0	0.084	0.004	0.056
	$\bar{r}_{v'v''}$ / Å	1.828	–	1.873	1.888	1.920
	$\lambda_{v'v''}$ / Å	3261.37	–	–	–	–
$v' = 6$	$q_{v'v''}$	0.123	0.025	0.057	0.014	0.059
	$\bar{r}_{v'v''}$ / Å	1.813	1.837	1.857	1.884	1.902
	$\lambda_{v'v''}$ / Å	3206.08	–	–	–	–
$v' = 7$	$q_{v'v''}$	0.092	0.060	0.017	0.053	0.014
	$\bar{r}_{v'v''}$ / Å	1.799	1.822	1.841	1.866	1.884
	$\lambda_{v'v''}$ / Å	3153.58	–	3322.59	–	–
$v' = 8$	$q_{v'v''}$	0.064	0.084	0	0.061	0.002
	$\bar{r}_{v'v''}$ / Å	1.785	1.807	–	1.851	1.883
	$\lambda_{v'v''}$ / Å	3103.01	3183.00	–	3352.64	–
$v' = 9$	$q_{v'v''}$	0.042	0.090	0.013	0.036	0.029
	$\bar{r}_{v'v''}$ / Å	1.772	1.794	1.817	1.836	1.860
	$\lambda_{v'v''}$ / Å	3054.71	–	–	–	–
$v' = 10$	$q_{v'v''}$	0.026	0.081	0.038	0.009	0.051
	$\bar{r}_{v'v''}$ / Å	1.759	1.780	1.802	1.820	1.845
$v' = 11$	$q_{v'v''}$	0.015	0.065	0.060	0	0.044
	$\bar{r}_{v'v''}$ / Å	1.746	1.767	1.789	–	1.830
	$\lambda_{v'v''}$ / Å	–	–	3113.22	–	–
$v' = 12$	$q_{v'v''}$	0.009	0.048	0.069	0.012	0.020
	$\bar{r}_{v'v''}$ / Å	1.733	1.754	1.776	1.798	1.816

The Franck–Condon factors of the band B$^1\Pi$ – X$^1\Sigma^+$ system of ^{123}SbP and ^{121}SbP species indicate that the following bands (0,0), (0,1), (0,2), (0,3), (1,0), (1,1), (1,3), (1,4), (15), (2,0), (2,2), (2,5), (2,6), (2,7), (3,0), (3,4), (3,7), (3,8), (4,1) and (4,3) are intense (F–C factors > 0.1), while all other bands are weak.

Since $r_e' > r_e''$, the r-centroid values increase with increasing wavelength, which is expected in the red degraded band system.

TABLE III. Franck–Condon factors, r-centroids and wavelengths of the $D^2\Pi – X^2\Pi$ system of ^{121}SbP

		$v'' = 0$	$v'' = 1$	$v'' = 2$
$v' = 0$	$q_{v'v''}$	0	0.003	0.012
	$\bar{r}_{v'v''}$ / Å	–	1.956	1.976
	$\lambda_{v'v''}$ / Å	–	3004.81	3077.90
$v' = 1$	$q_{v'v''}$	0.002	0.013	0.046
	$\bar{r}_{v'v''}$ / Å	1.926	1.944	1.963
	$\lambda_{v'v''}$ / Å	2892.01	2960.83	3031.78
$v' = 2$	$q_{v'v''}$	0.006	0.036	0.086
	$\bar{r}_{v'v''}$ / Å	1.914	1.933	1.951

TABLE IV. Franck–Condon factors, r-centroids and wavelengths of the $B^1\Pi – X^1\Sigma^+$ system of ^{123}SbP

		$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$	$v'' = 8$
$v' = 0$	$q_{v'v''}$	0.139	0.285	0.282	0.178	0.080	0.028	0.007	0.002	0
	$\bar{r}_{v'v''}$ Å	2.258	2.290	2.321	2.353	2.385	2.417	2.450	2.583	–
	$\lambda_{v'v''}$ Å	3560.68	3624.68	3690.59	3758.49	3827.17	–	–	–	–
$v' = 1$	$q_{v'v''}$	0.257	0.132	0	0.113	0.205	0.166	0.085	0.031	0.009
	$\bar{r}_{v'v''}$ Å	2.234	2.265	–	2.328	2.359	2.391	2.423	2.456	2.489
	$\lambda_{v'v''}$ Å	–	–		–	3771.68	3841.67	3913.83	–	–
$v' = 2$	$q_{v'v''}$	0.254	0	0.132	0.087	0	0.102	0.179	0.142	0.070
	$\bar{r}_{v'v''}$ Å	2.209	–	2.272	2.302	–	2.366	2.398	2.430	2.462
	$\lambda_{v'v''}$ Å	3463.38	–	3591.32	–	–	3784.17	3854.16	3926.31	–
$v' = 3$	$q_{v'v''}$	0.177	0.067	0.095	0.012	0.122	0.041	0.013	0.121	0.165
	$\bar{r}_{v'v''}$ Å	2.186	2.217	2.247	2.280	2.309	2.339	2.376	2.405	2.436
	$\lambda_{v'v''}$ Å	3417.38	–	–	–	3663.33	–	3797.30	–	–
$v' = 4$	$q_{v'v''}$	0.098	0.149	0.003	0.108	0.020	0.053	0.100	0.007	0.044
	$\bar{r}_{v'v''}$ Å	2.162	2.193	2.222	2.254	2.283	2.317	2.347	2.373	2.412
	$\lambda_{v'v''}$ Å	–	3429.40	–	–	–	–	–	–	–

If the sequence difference $\Delta\bar{r}_{v'v''} = \bar{r}_{v'+1,v''+1} - \bar{r}_{v',v''}$ was found to be constant (≈ 0.01 Å) for a given sequence, then it can be interpreted that the potential curves are not wide. In the present study, the sequence differences of all the considered band systems were found to be constant and are about 0.01 Å, which suggests that the potentials are not wide.

TABLE V. Franck–Condon factors, *r*-centroids and wavelengths of the $B^1\Pi - X^1\Sigma^+$ system of ^{121}SbP

		$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$v''=7$	$v''=8$
$v'=0$	$q_{v'v''}$	0.154	0.298	0.279	0.167	0.072	0.023	0.006	0.001	0
	$\bar{r}_{v'v''}$ Å	2.259	2.291	2.323	2.355	2.388	2.421	2.454	2.488	–
	$\lambda_{v'v''}$ Å	3559.28	3623.65	3689.68	3757.68	3827.79	–	–	–	–
$v'=1$	$q_{v'v''}$	0.271	0.117	0.003	0.132	0.210	0.157	0.075	0.026	0.007
	$\bar{r}_{v'v''}$ Å	2.234	2.265	2.301	2.330	2.362	2.394	2.427	2.460	2.494
	$\lambda_{v'v''}$ Å	3510.44	3572.74	–	3702.98	3771.02	3841.12	3913.41	–	–
$v'=2$	$q_{v'v''}$	0.255	0	0.145	0.072	0.006	0.121	0.182	0.132	0.061
	$\bar{r}_{v'v''}$ Å	2.209	–	2.273	2.304	2.340	2.369	2.401	2.434	2.467
	$\lambda_{v'v''}$ Å	3462.25	–	3585.16	–	–	3783.49	3853.59	3925.83	–
$v'=3$	$q_{v'v''}$	0.169	0.085	0.082	0.023	0.126	0.028	0.025	0.137	0.163
	$\bar{r}_{v'v''}$ Å	2.184	2.216	2.248	2.280	2.311	2.341	2.377	2.408	2.440
	$\lambda_{v'v''}$ Å	3416.16	3475.15	3535.83	3598.14	3662.44	–	3796.60	3866.70	3938.95
$v'=4$	$q_{v'v''}$	0.089	0.161	0	0.116	0.010	0.071	0.090	0	0.063
	$\bar{r}_{v'v''}$ Å	2.160	2.191	–	2.255	2.284	2.319	2.349	–	2.415
	$\lambda_{v'v''}$ Å	–	3428.13	–	–	–	–	–	–	–

The intensity ratio of the corresponding bands of isotopic molecules gives the abundance ratio of the molecules.[4] As the intensity is proportional to the Franck–Condon factor, Franck–Condon factor ratios also reflect the same.

From the present calculations, a Franck–Condon factor ratio of the isotopic species ^{123}SbP and ^{121}SbP of 1:0.9996 for the (0,0) band of the $B^1\Pi - X^1\Sigma^+$ system was obtained. The Franck–Condon factors ratio shows that the probability of transition and occurrence of isotopic molecules ^{123}SbP and ^{121}SbP are more or less the same in the same environment and allied sources.

TABLE IV. Molecular constants

Molecule	State	ω_e	$\omega_e x_e$ / cm^{-1}	r_e / Å	α_e	β_e
^{123}SbO	$A^2\Pi_{3/2}$	569.79	2.55	2.0336	0.001818	0.288028
	$X^2\Pi_{3/2}$	813.34	4.29	1.8227	0.0023781	0.358524
^{121}SbO	$C^2\Sigma$	570.00	3.52	1.997	0.002184	0.2991
	$D^2\Pi$	505.90	3.00	2.073	0.002092	0.2777
	$X^2\Pi_{3/2}$	814.07	4.3	1.8227	0.00238	0.358
	$X^2\Pi_{1/2}$	816.00	4.2	1.825	0.0022	0.358
^{123}SbP	$B^1\Pi$	393.10	1.624	2.314	0.0001	0.1273
	$X^1\Sigma^+$	499.24	1.624	2.204	0.0005	0.1402
^{121}SbP	$B^1\Pi$	394.00	1.632	2.313	0.0002	0.1278
	$X^1\Sigma^+$	500.07	1.632	2.206	0.0005	0.1406

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ИЗВОД

ПАРАМЕТРИ МОЛЕКУЛА SbO И SbP У ГАСОВИТОЈ ФАЗИ

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Franck–Condon фактори и *r*-центроиди, који су уско повезани са вероватноћом релативних вибрационих прелаза, одређени су нумеричком интеграцијом за траке $A^2\Pi_{3/2} – X^2\Pi_{3/2}$, $C^2\Sigma – X^2\Pi_{3/2}$ и $D^2\Pi – X^2\Pi$ система изотопског молекула SbO и за $B^1\Pi – X^1\Sigma^+$ систем изотопског молекула SbP, помоћу погодног потенцијала.

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