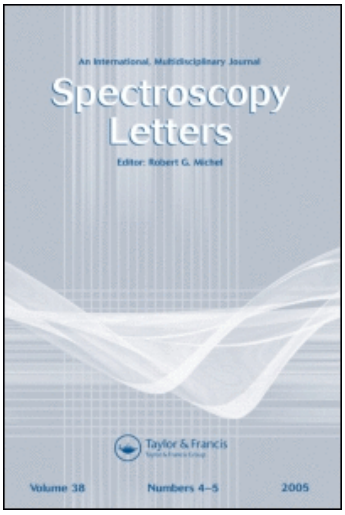

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Mean Amplitudes of Vibration for Some Linear Gold(I) Complexes

Enrique J. Baran[a]
[a] Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

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MEAN AMPLITUDES OF VIBRATION FOR SOME LINEAR GOLD(I) COMPLEXES

Key words: mean amplitudes of vibration, generalized mean square amplitudes, shrinkage effect.

Enrique J. Baran

Facultad de Ciencias Exactas, Universidad Nacional de La Plata. La Plata, Argentina.

Recently, Braunstein and Clark[1] described the synthesis and vibrational spectra of complexes containing the $AuCl_2^-$, $AuBr_2^-$ and AuI_2^- ions. In order to obtain a deeper insight into the vibrational properties of these anions it seems interesting to calculate, using the available spectroscopic data, values for the mean amplitudes of vibration and some related quantities.

The mean amplitudes of vibration at different temperatures were calculated using the "Method of the Characteristic Vibrations" proposed by A. Müller[2,3] (cf. also[4]). The results are shown in Table 1.

As a general rule, stronger bonds show lower values for the mean amplitudes of vibration[3]. Therefore, in this case we would expect lower amplitude values for $AuCl_2^-$ (with a force constant of 2.07 mdyn/Å for the Au-Cl bond[1]) than for $AuBr_2^-$ and AuI_2^- (with force constants of 1.86 and

1.65 mdyn/Å respectively[1]). Nevertheless, inspection of Table 1 shows immediately that this is not the case in the full temperature range. Only for temperatures above 300 °K the order of magnitude of the u-values shows the expected trend. In the 0 - 300 °K range the presence of the so called "low temperature anomaly" is evident. This effect is always observable in cases in which the amplitude values are governed essentially by mass effects rather than by the bonding forces[5,6].

The same effect has been observed in the isoelectronic mercury (II) halides[5]. A comparison of the pairs of isoelectronic species ($AuCl_2^-/HgCl_2$, $AuBr_2^-/HgBr_2$ and AuI_2^-/HgI_2) shows, furthermore, the expected decrease[3] of the mean amplitude values in going from the ion to the molecule, due to a corresponding increase of the force constant in the same direction. Mean amplitude values for the mercury-halo-

TABLE 1

Mean Amplitudes of Vibration (in Å) for $AuCl_2^-$, $AuBr_2^-$ and AuI_2^- at Different Temperatures.

Temp.(°K)	$AuCl_2^-$		$AuBr_2^-$		AuI_2^-	
	u_{Au-Cl}	$u_{Cl..Cl}$	u_{Au-Br}	$u_{Br..Br}$	u_{Au-I}	$u_{I..I}$
0	0.0406	0.054	0.0354	0.045	0.0338	0.041
100	0.0409	0.054	0.0367	0.047	0.0363	0.045
200	0.0442	0.059	0.0428	0.056	0.0442	0.057
300	0.0495	0.066	0.0497	0.066	0.0522	0.068
400	0.0549	0.074	0.0563	0.075	0.0594	0.078
500	0.0602	0.081	0.0623	0.083	0.0659	0.087

gen bonds at 300°K are: $HgCl_2$ = 0.0444; $HgBr_2$ = 0.0448 and HgI_2 = 0.0495 Å [3,5].

Another interesting and relevant comparison is that with the corresponding square planar $AuCl_4^-$ and $AuBr_4^-$ ions. The available data for these species[7] shows that at 0° and 300°K the mean amplitude values for the Au-X bonds are comparable with those of the corresponding AuX_2^- ions; also, the values for the non bonded X..X(long) distances are very close to the calculated values for the non bonded pairs in $AuCl_2^-$ and $AuBr_2^-$. This coincidences suggests similar bonding properties in both type of gold complexes. It has been previously shown[8] that analogous correlations also hold for square planar XY_4^- interhalogen anions and the corresponding linear XY_2^- species.

We have calculated also the values for the generalized mean square amplitudes at three temperatures, namely 0°, 300° and 500 °K, using the known relations between the $\sum$-matrix elements[9]. Results are presented in Table 2.

Finally, we have made an estimation for the Bastiansen-Morino shrinkage effect, which for three-atomic linear species is defined as[5]:

$$\delta = 1/2.R^{-1}.\sum_{22}$$

For R, the interatomic distances, we have assumed the following values: Au-Cl = 2.35 Å, Au-Br = 2.50 Å and Au-I = 2.70 Å.

At 300°K the following figures for the shrinkage effect are obtained: $AuCl_2^-$ = 0.0087 Å, $AuBr_2^-$ = 0.0109 Å and AuI_2^- = 0.0119 Å.

TABLE 2

Generalized Mean Square Amplitudes (in Å) for $AuCl_2^-$, $AuBr_2^-$ and AuI_2^-

Species	Distance	T(°K)	$\langle \Delta z^2 \rangle$	$\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$	Cross products
$AuCl_2^-$	Au-Cl	0	0.00165	0.00279	0
		300	0.00245	0.01028	0
		500	0.00362	0.01635	0
	Cl..Cl	0	0.00290	0	0
		300	0.00440	0	0
		500	0.00656	0	0
$AuBr_2^-$	Au-Br	0	0.00125	0.00248	0
		300	0.00247	0.01360	0
		500	0.00388	0.02250	0
	Br..Br	0	0.00202	0	0
		300	0.00436	0	0
		500	0.00692	0	0
AuI_2^-	Au-I	0	0.00114	0.00241	0
		300	0.00271	0.01609	0
		500	0.00435	0.02669	0
	I..I	0	0.00168	0	0
		300	0.00464	0	0
		500	0.00752	0	0

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