

INTERPRETATION OF THE INFRARED AND RESONANCE RAMAN SPECTRA OF LINEAR
MIXED VALENCE COMPOUNDS

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We consider a series of mixed valence ionic compounds of Pt or Pd consisting of independent parallel chains of square planar and octahedrally coordinated constituent molecules [1,2,3]. The vibrations of these molecules, when not in the chain, contain many different modes, mainly longitudinal, rotational, bending and transverse modes.

The Resonance Raman (RR) and Infrared (IR) spectra at room temperature of these compounds contain some modes that can be identified as the transverse, bending and rotational modes of the corresponding individual molecules. This is not so for the "longitudinal" modes (i.e. those along the chain direction) of the individual molecules. In fact the rest of the modes present in the spectra are not even in a one to one correspondence with them [4].

It is evident that while the coupling of the longitudinal vibrations of the molecules along the chain is significant, giving rise to collective (phonon) modes, (something not always recognized in the literature), the coupling of all other modes is not, and can be taken into account by introducing effective longitudinal spring constants, connecting the molecules along the chain.

In order to study the vibrations of such systems we therefore introduce a 1-D model consisting of a chain with an appropriate unit cell of four masses and the corresponding effective spring constants (Fig.1).

This model gives one acoustical and three optical modes and imposes the following selection rules on the $k=0$ frequencies of the optical modes:

$$\nu_2^2 + \nu_3^2 = (1+2B) \nu_1^2 \quad (1)$$

Table 1. The Three Longitudinal Lattice Modes, ν_i ; The Effective Spring Constants, f_1, f_2 ; and the Velocity of Sound, c'

Compound Label (+)	m_A	m_B	β	ν_1	ν_2	ν_3	f_1	f_2	c'
1	375	35	0.09333	316	340.87	48	12.86406×10^7	0.93349×10^7	4.2172×10^4
2	325	35	0.10769	304	322.24	44	10.01069×10^7	2.75884×10^7	6.2448×10^4
3	210	35	0.16667	295	316	73.79	10.16480×10^7	1.85983×10^7	6.2537×10^4
4	415	80	0.19277	175	198.79	54	8.83925×10^7	0.83297×10^7	2.7251×10^4
5	389	80	0.20565	170	198.9	35	8.61816×10^7	0.50924×10^7	2.7007×10^4
6	375	80	0.21333	179	212	23.54	9.79958×10^7	0.31984×10^7	2.5462×10^4

UNITS : m_A, m_B : Amu ν_i : cm^{-1} f_1, f_2 : Amu/cm^2 c' : cm/sec

The term used for frequency, ν , with units cm^{-1} is actually the wave number $\nu = \frac{1}{\lambda}$. The actual frequency, ν' , is given by $\nu' = \frac{c}{\lambda}$, where λ is the wavelength and c is the speed of light. The term used for spring constant is then modified by $f' = c^2 f$ (units: Amu/sec^2).

(+) The mass distribution in the unit cell (see Fig.1) of the compounds used is:

1	A_1, A_2	B_1, B_2	A_1, A_2	B_1, B_2
2	Pt+4D	Cl	Pt+2F+2Br	Br
3	Pt+2F+2Cl	Cl	Pt+2E+2Br	Br
4	Pt+4D	Cl	Pt+4D	Br

D: $\text{C}_2\text{H}_5\text{NH}_2$; E: NH_3 ; F: CH_2NH_2

$$1+\beta < \left(\frac{\nu_2}{\nu_1}\right)^2 < 1+2\beta \quad (2)$$

$$0 < \left(\frac{\nu_3}{\nu_1}\right)^2 < \beta, \quad (3)$$

where $\nu_i \equiv \nu_i(k=0)$, $i=1,2,3$ and $\beta \equiv \frac{m_x}{m_y}$ is the ratio of the smaller (halogen) mass to the larger mass in the unit cell (see Figure 1).

We further obtain [5] the effective spring constants, the dispersion relation for the acoustic and the three optical modes, we calculate how the system vibrates at $k=0$ and we obtain the velocity of sound by identifying our optical modes on the observed spectra [6,7,8,9].

The success of this scheme in interpreting the RR and IR spectra of all these compounds is in strong evidence that apart from the longitudinal phonons, all other modes (bending, rotational, etc.), are essentially not collective, but rather independent and localized on the individual molecules.

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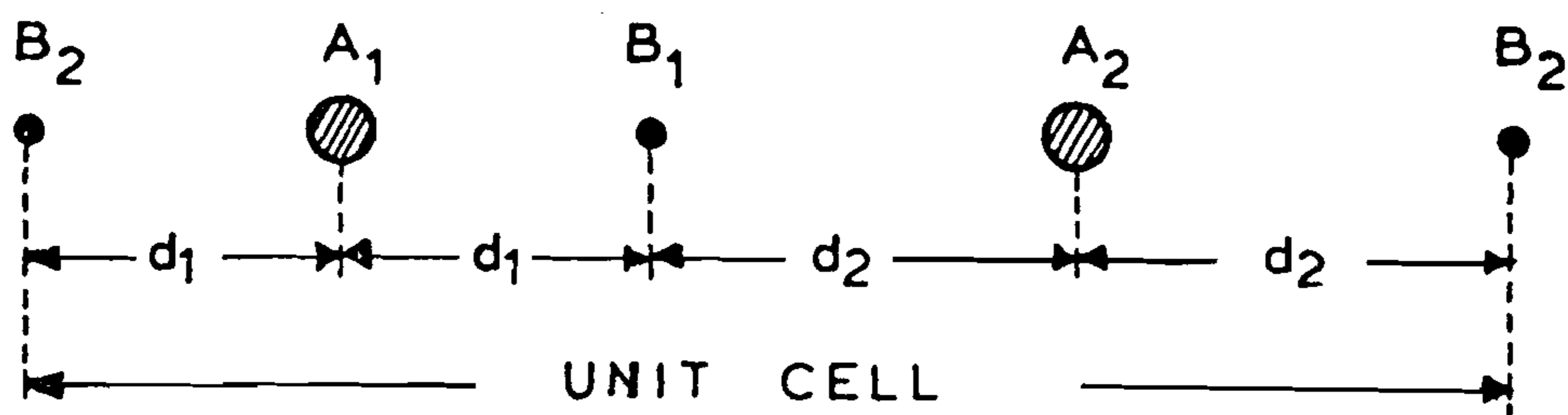


FIGURE CAPTION

Figure 1. Unit cell structure. Inter-ion distances $d_1 < d_2$. Effective spring constants f_1, f_2 (corresponding to d_1, d_2 respectively). Masses $m_{B_1} = m_{B_2} \equiv m_x$, $m_{A_1} = m_{A_2} \equiv m_y$, where x: Halogen ion (Cl, Br, I),

$$y: \begin{cases} G + 4D \\ G + 2E + 2x \\ G + 2F + 2x \end{cases}$$

and G: Pt or Pd, D: $C_2H_5NH_2$, E: NH_3 , F: CH_2NH_2 .