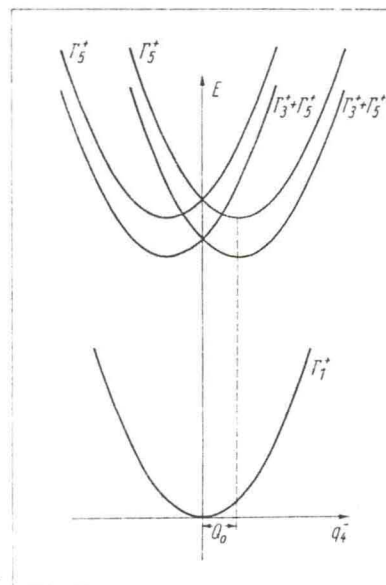


Fig. 6. Schematic plot of the energy versus interaction coordinate of the odd mode q_4^- (linear coupling)


The off-centre effect found in NaCl:Cu⁺ raises the question why no off-centre effect was found at the IR absorption of the resonance mode. Obviously the effect is only connected with the excited state I_5^+ of KCl:Ag⁺ which is distorted by the odd parity mode. This distortion may be described in terms of a relatively strong admixture of I_4^- electronic states to the I_5^+ -state which gives rise to a small off-centre displacement of the ion in the excited state. In NaCl:Cu⁺ the off-centre effect is bigger and is also found in the lower excited states. Fig. 6 shows this concept in a configuration coordinate model. The potential energy has been plotted versus one of the three symmetry coordinates q_4^- . We note that the modes described in Fig. 6 do not cause a broadening of the bands, but make the parity-forbidden transitions allowed. Q_0 denotes the off-centre displacement. The different energy parabolas of one excited state are degenerate at the inversion centre, where the ground state has minimal energy. This model explains the fact that no off-centre splitting of the IR resonance mode at low temperatures has been found by experiments.

In Section 2 we have seen that the first-moment change under stress was negligible. It was this fact which made a detailed analysis of the zeroth moment possible. But this lack of a stress splitting in NaCl:Cu⁺ and KCl:Ag⁺ is in contrast to the properties of other colour centres as F-centres, U-centres, and Tl⁺ ions. In all these systems a relatively strong splitting under I_3^+ - and I_5^+ -stress was observed. We conclude that the coupling of the excited states to I_3^- - and I_5^- -modes is small in NaCl:Cu⁺ and KCl:Ag⁺ and much too weak to cause a Jahn-Teller distortion. In such a case a second-order perturbation by odd modes (I_4^- and I_5^-) is no longer negligible and might cause an off-centre effect if there is a sufficiently strong coupling to the vibration of an impurity resonance mode. This seems to be the case for the A-band and the D-band of NaCl:Cu⁺ and for the D-band of KCl:Ag⁺. Stark effect measurements [4] and absorption measurements [1] indicate that the excited states of these bands have a strong ligand character which may increase the "orbital radius" and the polarizability of these states over those of the A- and B-bands in KCl:Ag⁺, and give rise to the observed stress effects.

5. Summary and Conclusions

The stress dichroism of the UV absorption bands in NaCl:Cu⁺ and KCl:Ag⁺ shows a change of the zeroth moment which is linear in stress, but no stress splitting. The dominant effect is explained by a splitting of the frequency of the IR active resonance mode. The splitting for I_5^+ -stress is smaller than 1/10 of the splitting for I_3^+ -stress which is in good agreement with measurements of the IR active mode under stress [11, 14].

he sign of the splitting $3\delta_3 =$ be positive. This is consistent of the IR resonance in KCl:Ag⁺. gnments for the transitions in and [9]. Besides this we obtain and (5.36 eV) in KCl:Ag⁺ which ratures. In the A-band of both sates the effect of the $I_1^+ \rightarrow I_3^-$ the B-band we obtain for the r strength $f_3/f_5 = 2.7$ which is d. [9]. The results agree in that oution.

term (17) is found to be 1 to , but it has a negative sign for at the quadratic electron-lattice gth of the transitions of Ag⁺ in

| $\langle Q^2 \rangle / \langle Q^2(0) \rangle$ | C | f_3/f_5 |
|--|-----------------------|-----------|
| $\times 10^{-2}$ *** | $+1.1 \times 10^{-2}$ | 1.2 |
| $\times 10^{-2}$ | -2.2×10^{-2} | — |
| 0 | $+2.3 \times 10^{-2}$ | 2.7 |
| 0 | $+0.8 \times 10^{-2}$ | — |
| $\times 10^{-2}$ | -2.7×10^{-2} | — |

effect into account (second term $\Delta|f|$ decreases with temperature. he A- and B-band of KCl:Ag⁺. bands of both systems show the for this reason we discuss these effect we calculate the δ_3 -effect as obtained from reference [11]. from the analysis of our measure- t we find $\Delta Q_0^2 = |\Delta Q_{10}^2 - \Delta Q_{10}^2|$ Ag⁺ and 9% for NaCl:Cu⁺ of the ance mode at $T = 0$ °K (Table 2). r behaviour should be expected. nds under high hydrostatic pres- Taking the values of $\Delta\omega/\omega$ and f_3/f_5 for the A-band in NaCl:Cu⁺ 2 into the expressions of Table 1 tical temperature dependence of).