Home Search Collections Journals About Contact us My IOPscience

The T×t Jahn-Teller problem: energy levels for large coupling

This article has been downloaded from IOPscience. Please scroll down to see the full text article. 1974 J. Phys. C: Solid State Phys. 7 L325 (http://iopscience.iop.org/0022-3719/7/17/001) View the table of contents for this issue, or go to the journal homepage for more

Download details: IP Address: 18.189.115.229 The article was downloaded on 27/10/2012 at 05:29

Please note that terms and conditions apply.

LETTER TO THE EDITOR

The $T \times t$ Jahn-Teller problem: energy levels for large coupling

M J Shultz and R Silbey

Department of Chemistry and Centre for Materials Science and Engineering, Massachusetts, Institute of Technology, Cambridge, Massachusetts, 02139, USA

Received 14 May 1974

Abstract. We have investigated the Jahn-Teller effect for strong coupling between a triply degenerate electronic state and a triply degenerate vibrational mode $(T \times t)$. We have derived analytic expressions for the lowest energy levels for finite but large coupling constant k, and have calculated the splitting between these levels. Our splitting between the lowest T and A states agrees well with Caner and Englman's (1966) fit of their numerical data.

The Jahn-Teller coupling between a triply degenerate electronic state and a triply degenerate vibrational mode $(T \times t)$ has been the subject of many investigations (Van Vleck 1939, Opik and Pryce 1957, Moffitt and Thorson 1957, Caner and Englman 1966, Englman *et al* 1970). Although the energy levels for infinite coupling strength k have been known since the calculation of the static potential surfaces by Van Vleck (1939) and Opik and Pryce (1957), the energy levels for finite but large k have not been thoroughly studied. Caner and Englman (1966) have done numerical calculations for $k \leq 2.5$ and have found the separation between the lowest singlet and triplet states to be $0.88k^2\omega \exp(-0.827 k^2)$ (or $0.8k^2\omega \exp(-0.8k^2)$ for large k). In this letter, we present an approximate calculation of the energy levels for k large but finite. Our calculation for the separation between the lowest singlet and triplet states agrees reasonably well with the above work, even though only the lowest vibrational state is taken into account.

We begin with the Hamiltonian written as

$$H = \omega(b_1 + b_1 + b_2 + b_3 + b_3 + \frac{3}{2}) + (k\omega/\sqrt{2}) [(b_1 + b_1^+) (c_2 + c_3 + c_3^+ c_2) + (b_2 + b_2^+) (c_1^+ + c_3^+ + c_3^+ + c_1) + (b_3 + b_3^+) (c_1^+ + c_2^+ + c_2^+ + c_1)]$$

where $b_i(b_i^+)$ destroys (creates) a vibration of type *i*, and $c_i(c_i^+)$ destroys (creates) an electronic state of type *i*. We transform to electronic and vibrational modes appropriate to a trigonal distortion in the direction I = (1,1,1) (Opik and Pryce). In this representation $H = H_0 + V$, where

$$H_{0} = \omega(\alpha_{1}+\alpha_{1} + \alpha_{2}+\alpha_{2} + \alpha_{3}+\alpha_{3} + \frac{\alpha_{3}}{2}) - (k^{2}\omega/6) (2\bar{c}_{1}+\bar{c}_{1} - \bar{c}_{2}+\bar{c}_{2} - \bar{c}_{3}+\bar{c}_{3}) 2$$

$$V = (k\omega/\sqrt{6}) [(\bar{c}_{1}+\bar{c}_{3}\theta + \theta + \bar{c}_{3}+\bar{c}_{1})(\alpha_{1}+\alpha_{1}+) + (\bar{c}_{1}+\bar{c}_{2}\theta + \bar{c}_{2}+\bar{c}_{1}\theta +)(\alpha_{2}+\alpha_{2}+) - \sqrt{2}(\bar{c}_{2}+\bar{c}_{2} - \bar{c}_{3}+\bar{c}_{3})(\alpha_{1}+\alpha_{1}+) - \sqrt{2}(\bar{c}_{2}+\bar{c}_{3} + \bar{c}_{3}+\bar{c}_{2})(\alpha_{2}+\alpha_{2}+)].$$

Here $\theta = \exp\left[\left(-\frac{3k}{\sqrt{6}}\right)(\alpha_3 - \alpha_3^+)\right]$, $\alpha_i(\alpha_i^+)$ destroys (creates) a vibration of type *i*, and $\bar{c}_i(\bar{c}_i^+)$ destroys (creates) an electronic state of type *i*. (In this notation, $|E_{\rm JT}| = \frac{2}{3}k^2$.)

To calculate the eigenfunctions near a trigonal distortion, we use the states appropriate to infinite k, which are localized in a single trigonal well (ie eigenfunctions of H_0), as basic states. We then calculate the wavefunctions to second order in V and find

$$\psi_{\mathrm{I}} = \left(\bar{c}_{1}^{+} - \frac{k}{\sqrt{6}} \sum_{n=0}^{\infty} \frac{(-3k/\sqrt{6})^{n}(\alpha_{3}^{+})^{n}}{n!(n+1+\frac{1}{2}k^{2})} (\bar{c}_{2}^{+}\alpha_{2}^{+} + \bar{c}_{3}^{+}\alpha_{1}^{+})\right) |0\rangle$$

$$E^{(2)} = \left(\frac{3}{2} - \frac{1}{6}\right)\omega - \frac{2}{3}k^{2}\omega + \theta(1/k^{2}).$$

(Note that we have a zero-point energy of $\frac{5}{6} + \frac{1}{2}$ instead of the exact $k = \infty$ value $(\frac{2}{3})^{1/2} + \frac{1}{2}$. First-order solutions localized in the other wells—ie at II=(-1, -1, 1), III=(-1, 1, -1), and IV=(1, -1, -1)—are similarly constructed.)

We now form appropriate (un-normalized) functions which transform as irreducible representations of the octahedral group by combining the lowest states of the four wells. For the lowest A_2 and T_1 states we have

$$\Phi_{\rm T_1} = \frac{1}{2} \begin{pmatrix} \psi_{\rm I} + \psi_{\rm II} - \psi_{\rm III} - \psi_{\rm IV} \\ \psi_{\rm I} - \psi_{\rm II} + \psi_{\rm III} - \psi_{\rm IV} \\ \psi_{\rm I} - \psi_{\rm II} - \psi_{\rm III} + \psi_{\rm IV} \end{pmatrix}$$

$$\Phi_{\rm A_2} = \frac{1}{2} (\psi_{\rm I} + \psi_{\rm II} + \psi_{\rm III} + \psi_{\rm IV}).$$

Using these states we calculate the matrix elements of the total Hamiltonian and find

$$E_{T_1}^{(1)} = E^{(2)} - (68/243)k^2\omega \exp(-8k^2/9)$$

$$E_{A_2}^{(1)} = E^{(2)} + (204/243)k^2\omega \exp(-8k^2/9)$$

and

$$E_{\rm A2}{}^{(1)} - E_{\rm T1}{}^{(1)} = (272/243)k^2\omega \exp(-8k^2/9).$$

If we neglect the first-order correction to the wavefunction, we find

 $E_{A_2}^{(0)} - E_{T_1}^{(0)} = (32/27)k^2\omega \exp(-8k^2/9).$

Finally, we note that if the approximate ground state wavefunctions localized in each trigonal well, the $\psi_{\rm I}$ etc, are chosen to be harmonic oscillator functions with the exact $k = \infty$ frequencies ω , $(\frac{2}{3})^{1/2} \omega$ and $(\frac{2}{3})^{1/2} \omega$, the approximate energies are

$$E_{T_1} = \left[\frac{5}{4} \left(\frac{2}{3} \right)^{1/2} + \frac{1}{2} \right] \omega - 0.315k^2 \omega \exp(-0.827k^2)$$

$$E_{A_2} = \left[\frac{5}{4} \left(\frac{2}{3} \right)^{1/2} + \frac{1}{2} \right] \omega + 0.945k^2 \omega \exp(-0.827k^2)$$

$$E_{A_2} - E_{T_1} = 1.26k^2 \omega \exp(-0.827k^2).$$

We note that these approximate results (valid asymptotically for $k \to \infty$) are very close to the numerical calculations for k < 3 of Englman and co-workers given above.

Since the present calculation is correct asymptotically for $k \to \infty$, we see that the major effect of the mixing of higher states (for large k) is to push the A and T states closer together, while keeping the same form for inter-well overlap.

We will report on the spectral line shapes and energies of higher states in a later publication with a more complete description of the calculation.

Note added in proof. Dr B Beers has informed us that he has also performed these calculations with similar results. We would like to thank him for pointing out a typographical error in our original manuscript.

References

Caner M and Englman R 1966 J. Chem. Phys. 44 4054 Englman R, Caner M and Toaff S 1970 J. Phys. Soc. Japan 29 306-10 Moffitt W and Thorson W 1957 Phys. Rev. 108 1251-5 Opik U and Pryce M H L 1957 Proc. R. Soc. A 238 425-47 Van Vleck J H 1939 J. Chem. Phys. 7 72