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J. Stanislawski, M. Prager, Wolfgang Häusler

Angaben zur Veröffentlichung / Publication details:

Stanislawski, J., M. Prager, and Wolfgang Häusler. 1989. "Coupled quantum rotors in dimethyl-tin-dichloride: the isotope effect." *Physica B: Condensed Matter* 156-157: 356-58.
[https://doi.org/10.1016/0921-4526\(89\)90677-7](https://doi.org/10.1016/0921-4526(89)90677-7).

COUPLED QUANTUM ROTORS IN DIMETHYL-TIN-DICHLORIDE: THE ISOTOPE EFFECT

J. STANISLAWSKI, M. PRAGER and W. HÄUSLER¹

Institut für Festkörperforschung der Kernforschungsanlage Jülich, Postfach 1913, D-5170 Jülich, Fed. Rep. Germany

¹*Institut für Theoretische Physik der Universität Erlangen, Glückstr. 6, D-8520 Erlangen, Fed. Rep. Germany*

The isotope effect of tunneling and librational states of methyl groups in dimethyl-tin-dichloride is explained on the basis of coupled pairs of quantum rotors. The temperature dependence of the tunnel splitting shows the scaling behaviour expected from theory.

1. Introduction

Tunneling molecules or molecular groups are usually well described in a single particle model [1]. Only in a few cases effects of coupling between rotors are observed [2–4]. In the simplest case of only two interacting one-dimensional rotors [2, 3] the eigenenergies of the system are determined by the Hamiltonian

$$H = H_1 + H_2 + W_{12}, \quad (1)$$

with the single particle terms

$$H_i = -B_i \frac{\partial^2}{\partial \varphi_i^2} + V_{3i} \cos 3\varphi_i,$$

$$B_i = \text{rotational constant}, \quad i = 1, 2, \quad (2)$$

and the interaction, which can be assumed to depend only on the difference of the rotational angles

$$W_{12} = W_3 \cos 3(\varphi_1 - \varphi_2). \quad (3)$$

For crystallographically equivalent ($V_{31} = V_{32}$) and identical ($B_1 = B_2$) particles the calculations [5] yield a librational ground state consisting of 4 tunneling sublevels. In the case of $(\text{CH}_3)_2\text{SnCl}_2$ the crystallographic structure [6] shows the presence of pairs of methyl groups. Because of a strong single particle potential the structure of the broadened tunneling transition cannot be resolved like for lithium acetate [2]. All spectra can be described consistently with

potential parameters

$$(V_3, W_3) = (17.5, 10.9) \text{ meV}. \quad (4)$$

The interaction counteracts the single particle potential as expected from the structure [3]. – Attributing the width of the tunneling line to inhomogeneous broadening, however, the neutron spectra can be fitted by including an unusually [8] strong $V_6 \cos 6\varphi$ term in the rotational single particle potential [7]. An unambiguous test of the importance of coupling is possible by studying the isotope effect: especially in the partially deuterated compound the single particle and the coupling model show different scaling behaviour. – Finally the temperature dependences of the tunnel splitting in the three compounds is compared with existing theories on the basis of the observed isotope effects.

2. Experimental

The (partially) deuterated compounds were prepared by some modified technique, described in the literature [9, 10]. The tunneling transitions were measured with the back-scattering spectrometers of the ILL. Librational states and other phonons were recorded with a thermal time of flight spectrometer.

3. Results and discussion

3.1. CH_3 – CD_3 pairs

Since the interacting methyl groups belong to

different molecules, $\text{CH}_3\text{--CD}_3$ pairs can most easily be created by solving protonated molecules in a deuterated matrix. Various such samples and others containing $(\text{CH}_3)(\text{CD}_3)\text{SnCl}_2$ give almost identical result. This shows that the intramolecular methyl–methyl interaction is negligible. The tunnel peak is shifted to $57.8\text{ }\mu\text{eV}$ compared to $49\text{ }\mu\text{eV}$ in the fully protonated material and considerably broadened (fig. 1(b)), partly because there is a finite probability of finding $\text{CH}_3\text{--CH}_3$ pairs, partly because of sample inhomogeneities. Without interaction the tunnel splitting should not have changed at all. In real systems the stronger localization of deuterons leads often to a shallow lattice contraction and thus an increase of the rotational potential, i.e. a decrease of $\hbar\omega_i$ [11]. This effect is also found in the present system: The dash-dotted line in fig. 1(b) which represents the contribution of fully protonated pairs is found at smaller tunnel splittings ($46\text{ }\mu\text{eV}$) than in the pure protonated compound. Consistently the tunnel peak of the

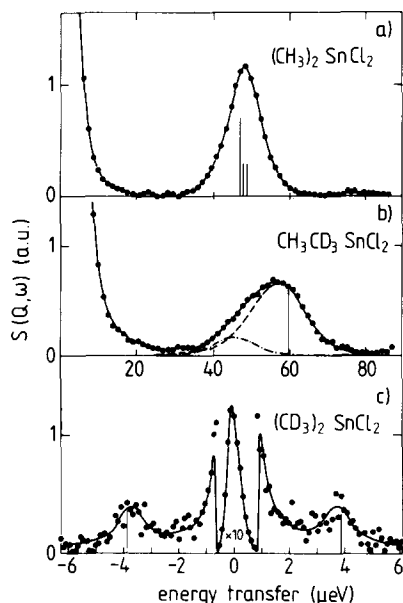


Fig. 1. Tunneling spectra of the three isotopomers of dimethyl-tin-dichloride. Spectrometers at the ILL and energy resolutions: IN13, $\Delta E = 8\text{ }\mu\text{eV}$ (a and b); IN10, $\delta E = 0.55\text{ }\mu\text{eV}$ (c). Solid lines: Fits with Gaussians. Bars: transition energies calculated from the Schrödinger equation (1) for the potential parameters (4). Other lines (b): dash-dotted – contribution of $\text{CH}_3\text{--CH}_3$ pairs; dashed – contribution of $\text{CH}_3\text{--CD}_3$ pairs.

mixed methyl pairs is also found at smaller energies than calculated for the potential (4) (bars in fig. 1). The overall shift to larger energies, however, is a sure proof of coupling. – The coupling model also explains the considerably reduced librational energy of 4.5 meV in $(\text{CH}_3)(\text{CD}_3)\text{SnCl}_2$ (5.5 meV in $(\text{CH}_3)_2\text{SnCl}_2$) (fig. 2). In a single particle picture no shift or an increase (see above arguments and ref. [11]) is expected. The V_3/V_6 potential cannot explain any of the presented observations.

3.2. $\text{CD}_3\text{--CD}_3$ pairs

For the fully deuterated compound the predictions of the coupling and the single particle model are not very different. The predictions of the coupling model are closer to the experimental results, however. The observed tunnel splitting ($3.74\text{ }\mu\text{eV}$) is again smaller than the one calculated from the coupling model ($3.88\text{ }\mu\text{eV}$) on the basis of the potential parameters (4).

3.3. Temperature dependence of tunnel splittings

The different eigenenergies of the coupled rotor systems in the deuterated systems should

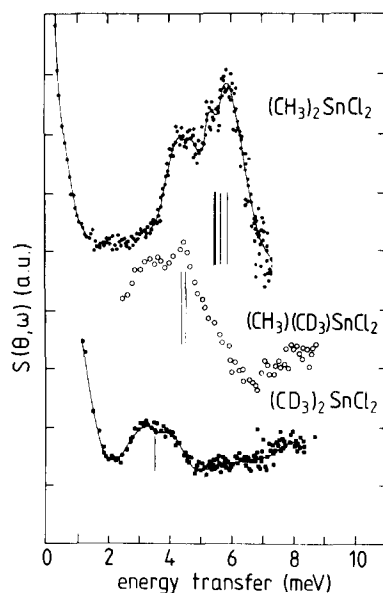


Fig. 2. Spectra taken in the energy regime of the first excited librational state from the three isotopomers of dimethyl-tin-dichloride. Spectrometer: SV22 in Jülich, $\delta E = 0.4\text{--}0.6\text{ meV}$. Solid lines are guides to the eye only. Bars: calculated transition energies as in fig. 1.

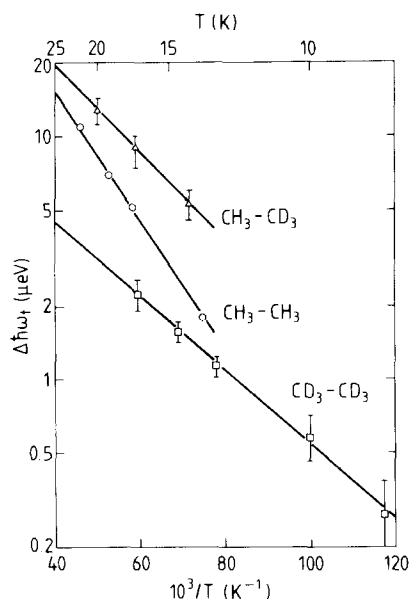


Fig. 3. Temperature dependence of the shift of the tunnel splitting $\hbar\omega_t(T) - \hbar\omega_t(0)$ for the three isotopomers of dimethyl-tin-dichloride. The parameters of the three Arrhenius lines are given in table I.

Table I

Average tunnel splitting and parameters for its temperature dependence (5) for the three isotopomers of dimethyl-tin-dichloride.

	$(\text{CH}_3)_2$	CH_3CD_3	$(\text{CD}_3)_2$
$\hbar\omega_t$ [μeV]	49	57	3.88
A [meV]	0.186	0.100	0.018
E_s [meV]	5.3	3.5	3.0

cause a different temperature dependence of the tunneling transitions [12]. Fig. 3 show the experimental results. The tunnel splittings in all three materials shift with temperature according to Arrhenius laws

$$\Delta\hbar\omega = A \exp(-E_s/kT). \quad (5)$$

The characteristic parameters are given in table I. The activation energy is almost equal to the lowest librational excitation of the respective system and decreases thus with increasing deu-

teration. For the first time it is shown here that the prefactor in the deuterated system is about an order of magnitude smaller than in the (partially) protonated system. The theory [12] predicts such a behaviour since the shift is proportional to the tunnel splitting in the first excited librational state, which shows an isotope effect similar to that observed for the ground state splitting.

4. Conclusion

It has been shown by comparing rotational spectra (tunneling, librations) of protonated, partially and fully deuterated dimethyl-tin-dichloride, that the methyl groups exist as coupled pairs. The different shifts of the tunnel transitions with temperature can be explained on the basis of existing theories and the observed scaling behaviour of the eigenenergies in a rotational potential almost unchanged with interaction.

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