Thermodynamics of Jahn-Teller molecules

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Introduction

The vast majority of molecules and radicals important in combustion or atmospheric kinetics have relatively simple electronic and vibrational structures. Most stable molecules have singlet ground states with excited states that are close to 100 kcal/mol higher in energy. The vibrational structure of most molecules can be readily described using the simple harmonic oscillator model, possibly with some anharmonic corrections. The thermodynamics of these molecules can be easily handled using standard statistical treatments. While the chemistry of free radicals is quite different from that of molecules, their treatment under statistical thermodynamics is for the most part very similar to that of molecules.[1]

A class of molecules for which the above statements do not hold are those subject to the Jahn-Teller effect. These molecules have by necessity open-shell electronic structures with orbitally degenerate ground states. Two important combustion radicals, the methoxy radical, CH_3O,[2] and the cyclopentadienyl radical, C_5H_5,[3] have ^2E ground states that are subject to a Jahn-Teller distortion. While these two radicals have been investigated for over 50 years, the details of their vibrational structure have only been resolved in the last 5 years.

Quantum mechanics of Jahn-Teller states

The quantum mechanics of Jahn-Teller molecules has been examined in excruciating detail elsewhere.[2] For the purposes of this paper, only a few key points will be summarized.

(1) The quantum mechanis of a Jahn-Teller molecule are most efficiently described via a few small perturbations to the Hamiltonian appropriate for a ^2E state. The molecule is distorted from the higher symmetry geometry, but this distortion is dynamic, not static, for CH_3O and C_5H_5. To analyze the spectroscopic energy levels based on a Hamiltonian appropriate for the distorted geometry would require many more correction terms than the Hamiltonian derived from the higher symmetry geometry.

(2) For most molecules, the Hamiltonian for the vibrational energy levels is separable from the electronic and spin Hamiltonians. This is not the case for ^2E states. Thus, the partition function cannot in general be written as the product of the individual components ($q_{JT} \neq q_{spin}*q_{elec}*q_{vib}$).

In the absence of any Jahn-Teller coupling, q_{elec} is equal to the orbital degeneracy of the state; i.e., 2 for a ^2E state. If the spin-orbit coupling is small, like in C_5H_5, then q_{spin} can be separated out as $q_{spin}=2*S+1$ for all temperatures. The entire spin-vibrational-electronic Hamiltonian must be diagonalized in order to compute q_{JT}. Rotational and translational contributions can still be separated, to make $q_{tot} = q_{JT}*q_{rot}*q_{trans}$.

(3) For non-zero spin-orbit coupling, like in CH_3O, all vibrational energy levels are split into pairs. The splitting energies vary widely, with a general diminishment to zero as the total internal energy is increased. For the purposes of statistical thermodynamics, the spin-orbit splitting of the zero-point level can be used to compute q_s using the normal Boltzman equation.

(4) The vibrational energy levels are not evenly spaced, but instead have very irregular spacings for the first few thousand cm^{-1} of internal energy. However, they maintain intervals that are of the order of vibrational intervals (a few 100 cm^{-1}), rather than spacings of rotational energy levels (a few cm^{-1}). To compute the partition function of the Jahn-Teller vibrations requires a numerical calculation of the energy levels and a numerical calculation of the partition function based on those energy levels.

Conclusions

Several qualitative conclusions regarding the statistical thermodynamics of Jahn-Teller molecules can be made. A quantitative description will be given in the full paper to be published.

(1) The vibrational modes of a Jahn-Teller molecule are not harmonic, but the harmonic approximation may give a reasonably accurate partition function, especially at high temperatures.

(2) Treatment of the electron spin must be included in the thermodynamic calculation. For C_5H_5, the spin-orbit coupling is essentially zero, giving a full contribution of R ln 2 to the entropy at all temperatures. For CH_3O, it is small (60 cm^{-1}), making a difference only at low temperatures. For sulfur-centered radical such as CH_3S, the 250 cm^{-1} spin-orbit splitting makes a larger difference.

(3) The use of the phrase "pseudo-rotation" to describe the motion of a Jahn-Teller molecule is misleading. This phrase implies that the degrees of freedom that account for the Jahn-Teller distortion can be treated by some type of rotational function. In actuality, what is "pseudo-rotating" about the Jahn-Teller moat is not the nuclei, but the electronic wavefunction. Thus, the energy level spacings of the Jahn-Teller distortion are closer to that of a vibration rather than any type of rotation.

(4) The electronic degeneracy must be included in the entropy via an R ln 2 contribution. At low temperatures the contribution is not exactly R ln 2, and but must be computed from the full numerical diagonalization of the Hamiltonian. The commonly used *ab initio* find a singly degenerate state at a distorted geometry, and a singly degenerate excited state that usually is a maximum on the surface. If the excited state is omitted from the partition function, then the computed entropy will be low.

(5) *ab initio* calculations of the minimum can be used as a reasonable approximation to the full Jahn-Teller statistical thermodynamics, provided that the entropy due to the excited states is included. The errors of this approximation are largest at lower temperatures, and diminish significantly at combustion temperatures.

References

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