The effects of torsion–vibration coupling on rotational spectra: Toluene reinterpreted and refitted

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ABSTRACT

A re-examination of rotational line positions for toluene is reported, motivated by the recent observation that the methyl internal rotor states are perturbed by torsion–vibration coupling to vibrational mode M_{20} (Gascooke et al., 2015). We demonstrate that the data can be fit equally well including or excluding torsion–vibration coupling. The torsion–vibration model required to account for the torsional band positions is thus shown to be consistent with the rotational line positions reported. It is found that including torsion–vibration coupling leads to changes in the values of the rotational and torsional constants, most significantly for A_F, A_F', F and V_6, as well as the higher order constants, with those involving powers of m, K and their cross-terms most affected. Expressions for these effects are provided based on a perturbation expansion, which shows the links between the two models. A primary indicator for the presence of torsion–vibration coupling is A_F' being significantly different to the rotational constant for the frame, A_F, and changing with m. Examination of published A_F'/A_F ratios for several substituted toluenes suggests that torsion–vibration coupling is widespread in such molecules. Torsion–vibration coupling has been directly observed through local perturbations to torsional levels in substituted toluenes with both 3- and 6-fold torsion potentials, indicating that it will also affect rotational and torsional constants in molecules with a 3-fold barrier. This indicates that the assumption that the small amplitude vibrations can be ignored when considering the large amplitude methyl rotation requires reassessment.

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1. Introduction

Internal rotation is an example of large amplitude motion that is regarded as being well understood spectroscopically, with significant progress having been made in analyzing rotational spectra for molecules with an internal rotor and fitting them to within experimental uncertainties. In 2010 Kleiner reviewed and compared the various approaches taken to solving this problem, which is treated in terms of a torsion–rotation interaction [1]. Groner subsequently provided an overview of the theoretical underpinnings of the ERHAM code, which applies to molecules where there are one or two internal rotors [2]. Interest in this problem is motivated by the development of astronomical facilities for making observations up to the THz and far-infrared region, where internal rotors often have many transitions [1,2]. Precise calculations of spectral line frequencies are required to enable known species to be identified and new species discerned. Spectra involving highly excited torsional states are excellent probes of the temperature in the

environment studied [1]. Consequently, accurate calculations of transitions involving such states are highly desirable.

The methyl rotor is the most widely studied internal rotor. While for many molecules the methyl rotor involves a 3-fold torsional potential (i.e. the potential repeats three times during a 2π rotation of the methyl group thus generating a cos 3α term), there is an important class of molecules that involve a 6-fold potential and hence a cos 6α term. This potential arises when the rotor is attached to a frame with C_{2v} symmetry, toluene being a textbook example. Successful analysis of toluene's rotational spectrum is an important test for the development of appropriate Hamiltonians and their corresponding fitting algorithms for this class of molecule.

Recently, we reported dispersed fluorescence spectra revealing the torsional bands, i.e. methyl rotation bands, associated with 0_0 and the lowest frequency vibrational mode, M_{20} [3]. (The nomenclature introduced by Gardner and Wright is used to label the vibrational modes [4,5].) These spectra show that the methyl torsional states are perturbed by a strong torsion–vibration coupling between 0_0 and 20_1, and subsequent dispersed fluorescence from higher S_1 torsional bands has confirmed this interaction between methyl rotation and the lowest vibrational mode by observing

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the mixed nature of the most strongly perturbed S_0 states [6]. This coupling is an example of the interaction of a small amplitude vibration, M_{20}, with large amplitude motion, methyl internal rotation. It not only shifts the torsional band positions, it also alters the rotational states. Using the example of the $20_1^0 m_4^1$ rotational contour observed in dispersed fluorescence, we demonstrated that a proper account of the rotational structure of torsional states requires the inclusion of torsion–vibration coupling [3]. (Here m is the quantum number describing methyl rotor excitation.) The influence of torsion–vibration coupling on the torsional levels of 0_0 increases with increasing m (at least up to $m = 7$) due to the separation of the coupled levels decreasing. Consequently, the effects of torsion–vibration coupling on the rotational structure and spectrum will become more pronounced with increasing torsional excitation, making models that exclude it increasingly unreliable as m increases. We are not aware of any current models used in the analysis of rotational spectra of torsional bands that explicitly incorporate torsion–vibration coupling as it is assumed that the lower torsional states can be approximated to be independent of the small amplitude vibrations.

Interestingly, previous work has provided successful analyses of toluene rotational spectra that take no account of torsion–vibration coupling. Kisiel et al. [7] reported a study of rotational transitions in toluene that extended the earlier data of Rudolph et al. [8] to higher J states with the aim of facilitating the accurate detection of toluene in millimeter wave radio-astronomy. While they fitted rotational transitions within $m = 0$, the authors noted that they had measured lines for torsional states up to $m = 6$ and undertaken preliminary fitting. Recently, Ilyushin et al. [9] reported the analysis of rotational transitions for toluene torsional states up to $m = 3$ using a new torsion–rotation Hamiltonian as they had found that existing programs were unable to do so. Their analysis produced a set of constants of impressive precision: 372 line frequencies for the torsional levels $m = 0, 1, 2$ and $3(\pm)$ with $J \leqslant 30$ and $K_a \leqslant 12$ were fit to 28 constants with a root mean square (RMS) value for the residuals, i.e. the differences between the predicted transition frequencies and experiment, of 7.4 kHz. The torsional barrier height was reported to be 4.83783617(94) cm^{-1}, which compares with a barrier height of 1.57 cm^{-1} determined from our analysis of the torsional band positions [3].

We have the interesting situation where torsion–vibration coupling is required to explain the torsional band positions and rotational contours seen in dispersed fluorescence, while the rotational line positions measured in high precision rotational spectra can be accurately reproduced without recourse to this effect. Clearly, there is a need to resolve this situation.

In this paper we explore how these two interpretations can be reconciled. We have shown previously that the torsion–vibration coupling model can reproduce the positions of the four microwave transitions that are most sensitive to V_6 [3,10]. Here we report an extension of this torsion–vibration analysis to the data set reported by Ilyushin et al. in their recent analysis [9]. By first considering fits to low J transitions using a low order Hamiltonian, we discuss the effects that the torsion–vibration interactions have on the constants. This leads to an analysis of how torsion–vibration coupling affects the torsion–rotation Hamiltonian, and we show that it alters the values of key rotational constants and methyl torsional constants and leads to higher order torsion–rotation terms. The effects of torsion–vibration coupling on the full set of constants used by Ilyushin et al. are explored by examining the dependence of the constants on the value of the torsion–vibration coupling constant. Having established this foundation, we present the results of a torsion–vibration coupling fit to the full data set that was fitted by Ilyushin et al. We then explore the effects of torsion–vibration coupling on spectra for higher m to illustrate the types of changes

in the primary constants expected for these states. Finally, we consider data for related molecules that suggest that torsion–vibration coupling is likely to be widespread.

2. Low order Hamiltonian, initial fits and changes to constants

In this section we examine the differences between the constants determined by fits to the experimental line positions including and excluding torsion–vibration coupling. A low order Hamiltonian with few parameters is used so that the dominant changes in the constants resulting from the inclusion of torsion–vibration coupling are exposed. The constants included are what might be regarded as the "primary constants" required to specify the rotational and torsional energies. These constants relate to physical characteristics of the molecule, specifically its geometry. The higher order constants effectively adjust the energy to account for centrifugal distortion and various higher order interactions and, since they generally involve a dependence on higher powers of J and/or K (*vide infra*), the low order Hamiltonian is expected to be most appropriate at low J [11]. Almost half of the transitions used in Ilyushin et al.'s analysis [9] involved states with $J \leqslant 6$ and these are the data used in this initial analysis. Having established the changes that are occurring, we examine the Hamiltonian to identify the effect of torsion–vibration coupling on the energy levels and hence constants.

2.1. The low order Hamiltonian

The Hamiltonian used for the initial analysis is: [10–13]

$$H = H_{Rotor} + H_{AsymmetricTop} + H_{Torsion-Rotation} \tag{1}$$

where

$$H_{Rotor} = Fp^2 + \frac{1}{2}V_6(1 - \cos 6\alpha) \tag{2}$$

$$H_{AsymmtericTop} = A_F P_z^2 + B P_x^2 + C P_y^2 \tag{3}$$

$$H_{Torsion-Rotation} = -2A_F' p P_z \tag{4}$$

Here F is the reduced rotational constant associated with the internal rotor, $F = \frac{\hbar^2 (I_F + I_M)}{2 I_F I_M}$, where I_F and I_M denote the moments of inertia for the phenyl frame and methyl group, respectively. V_6 denotes the barrier height, p denotes the angular momentum associated with the methyl internal rotation, and P_x, P_y and P_z denote the angular momenta of the molecule about the x-, y- and z-axes (in the z direction it excludes the internal rotor, which is assumed to lie on the z axis). A, B and C denote the usual rotational constants with, in the case of A, the subscript F indicating that the constant relates to motion of the phenyl frame rather than the complete molecule. The prime on A_F in Eq. (4) indicates that this may be different to A_F for the phenyl frame [14]. (In the notation of Ilyushin et al. $A_F' \equiv \rho F$ [9].) This difference has been interpreted as a precession of the rotor during torsional motion [13,15].

The torsion–rotation Hamiltonian is solved by setting up the problem in terms of basis states $|\underline{m}, J, K\rangle$ that are a product of free rotor and symmetric top functions and diagonalising the resulting matrix. Here $\underline{m}$ is the quantum number associated with free rotation of the methyl rotor, with the free rotor wavefunctions being written as $\psi = \frac{1}{\sqrt{2\pi}} \exp(i\underline{m}\alpha)$, where α is the angle of rotation of the methyl group, and J and K are the usual quantum numbers associated with molecular rotation [16]. In the notation used here both $\underline{m}$ and K are signed. The H_{Rotor} term is independent of J and K and leads to the following non-zero matrix elements [17]: