LETTERS TO THE EDITOR

COMMUNICATIONS

Methyl torsional barriers in different electronic states. Simultaneous determination from the rotationally resolved fluorescence excitation spectrum of a large molecule

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Hindered internal rotation of methyl groups has been the subject of considerable interest in thermodynamics, in conformational analysis and, increasingly, in intramolecular dynamics. For example, the coupling of methyl torsional modes with other vibrational motions can provide the level mixing that is a necessary prerequisite to energy flow in nonequilibrium states of isolated molecules.[1] The degree of such mixing, and thus the rate and extent of energy randomization, is a sensitive function of the torsional barrier heights and the relative displacements of the potential surface(s) along different coordinates. In this report, we describe high resolution fluorescence excitation (FE) experiments on the 0_0^0 band of the $S_1 \leftarrow S_0$ transition of 1-methylnaphthalene (1MN) which demonstrate that these properties can be determined from its rotationally resolved electronic spectrum.

Our experiments were performed in the collision-free environment of a molecular beam using a newly constructed laser spectrometer, described elsewhere.[2] A heated (250 °C) sample of 1MN was seeded in 2.6 atm of Ar, expanded through a 240 μm quartz nozzle, skimmed twice, and probed 100 cm downstream of the nozzle using a tunable CW laser operating in the UV. The laser (FWHM < 1 MHz) was centered at the origin of the 0_0^0 band of 1MN at 31 773.573 $\pm$ 0.002 cm^{-1} ($\sim$315 nm) and scanned over a range of up to $\pm$ 100 GHz at a speed of 58.4 MHz s^{-1}. Calibrated and power normalized FE spectra were recorded using a photon counter and MASSCOMP computer system with a digital accuracy of 372 kHz. The entire band, which is an a/b hybrid band with $\sim$80% a character, spans $\sim$170 GHz at $T_r \sim 25$ K and consists of 3000 + lines, each with a FWHM of 3–4 MHz, all of which have been assigned.

Figure 1 shows a small portion ($\sim$600 MHz) of the spectrum at full experimental resolution. The strong lines in this region are a-axis, parallel-type, Q-branch transitions involving high K_{-1} states and obeying the selection rules $\Delta J = \Delta K_{-1} = 0$. We observe that (a) each rovibronic line is split into two components, separated by $\Delta \nu_1 = 50.3 \pm 0.2$ MHz, (b) the two components have approximately the same intensity, and (c) one of the two components is further split into a doublet, with a separation $\Delta \nu_2$ that increases linearly

with K_{-1}, $\Delta \nu_2 = (0.493 \pm 0.02) K_{-1}$ MHz. All lines in the spectrum exhibit the same behavior. Observation (a) is explained by the tunneling motion of the methyl group. That $\Delta \nu_1$, which is equal to the difference in the torsional A–E level separations in the two electronic states, is small and essentially constant throughout the spectrum shows that the two barriers are very similar. Observation (b) requires that the equilibrium conformations of the methyl group in S_0 and S_1 are also very nearly the same. But, despite these similarities, observation (c), which is explained by the weak coupling of internal and overall rotation,[3] requires that the magnitude of this coupling be different in the two electronic states.

We now show that a quantitative comparison of these observations makes possible a unique determination of the barrier heights in *both* S_0 and S_1. The effective rotational
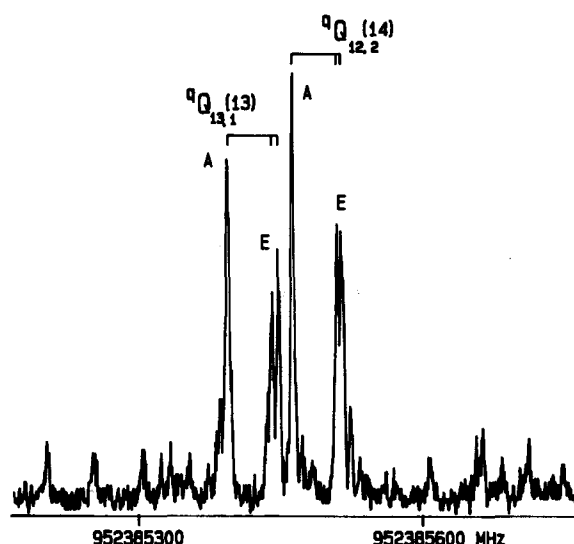

FIG. 1. A 600 MHz portion of the rotationally resolved fluorescence excitation spectrum of the 0_0^0 band of the $A\ ^1A' \leftarrow X\ ^1A'$ ($S_1 \leftarrow S_0$) transition of 1-methylnaphthalene, at $\sim$315 nm. Individual A and E lines are labeled according to the convention $^{\Delta K_{-1}} \Delta J_{K''_{-1}, K''_{+1}} (J'')$. The FWHM of each line, recorded with a digital accuracy of 372 kHz, is 3 MHz.

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Hamiltonian for the A torsional levels is, in the (PAM) high-barrier approximation,[4]

$$\hat{H}_A = FW_A^{(0)} + A_A P_a^2 + B_A P_b^2 + C_A P_c^2. \qquad (1)$$

Here, $FW_A^{(0)}$ is the zero-order torsional energy, P_a, P_b, and P_c are the components of the total angular momentum in the inertial frame, and A_A, B_A, and C_A are the effective rotational constants, given by $A_A = A + FW_A^{(2)}\rho_a^2$, etc., where the $W_A^{(2)}$ are second-order torsion–rotation perturbation coefficients and the rest of the symbols have their usual meaning.[5] Equation (1) is a quasi-rigid-rotor Hamiltonian so the A lines can be treated as (perturbed) normal asymmetric rotor spectral lines. But the corresponding expression for E torsional levels contains, in addition, the first-order correction terms

$$\hat{H}_E^{(1)} = FW_E^{(1)}(\rho_a P_a + \rho_b P_b + \rho_c P_c) \qquad (2)$$

leading to a deviation from rigid-rotor behavior. The high J, high K_{-1} levels of a near-prolate asymmetric top are doubly degenerate. The torsion–rotation coupling lifts this degeneracy and produces a small splitting of the E lines because the barriers in the two states are not exactly the same. Since $\Delta K_{-1} = 0$ for a-axis transitions, the separation of the E lines is

$$\Delta\nu_2 = 2F\Delta W_E^{(1)}\rho_a K_{-1}, \qquad (3)$$

where $\Delta W_E^{(1)} = |W_E^{(1)}(S_1) - W_E^{(1)}(S_0)|$. Comparing this result to that measured experimentally yields $\Delta W_E^{(1)} = 0.000\,443 \pm 0.000\,018$. The difference in perturbation coefficients $\Delta W_E^{(1)}$ depends mainly on the difference in barrier heights, so the values of V_3 for each electronic state cannot be determined from these data alone. But there is only one set of V_3 values which produce splittings $\Delta\nu_1$ and $\Delta\nu_2$ that *simultaneously* agree with experiment; these are $V_3(S_0) = 295.2$ and $V_3(S_1) = 292.6$ cm^{-1}. The difference in V_3 values cannot be in error by more than 0.3 cm^{-1} since $\Delta\nu_1$ is known to within 0.4%. But their absolute values could be in error by as much as 20%, owing to possible errors in our estimates of F, ρ_a, and $\Delta\nu_2$.[6] These conclusions are not

changed by the addition of small V_6 terms to the hindering potential of either or both electronic states.

The technique described here is extremely sensitive to changes in the torsional barriers of methyl groups, changes that might occur on electronic[7] and/or vibrational[8] excitation of large molecules to which the hindered rotors are attached. In the case of the zero-point vibrational levels of S_0 and S_1 1MN, the difference in V_3 values is surprisingly small. Apparently $S_1 \leftarrow S_0$ excitation produces little change in the relative C_1–C_2 and C_1–C_9 π-bond orders. But the changes are much larger in other cases, particularly those involving excitation of nonbonding electrons.[9] Further studies of these effects and their possible role in intramolecular dynamics are in progress. This work has been supported by the NSF (CHE-8814412 and INT-84101313).

[1] See, for example, D. B. Moss, C. S. Parmenter, and G. E. Ewing, J. Chem. Phys. **86**, 51 (1987).
[2] W. A. Majewski, D. F. Plusquellic, and D. W. Pratt, J. Chem. Phys. (in press).
[3] D. R. Herschbach and J. D. Swalen, J. Chem. Phys. **29**, 761 (1958).
[4] W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, 3rd ed. (Wiley-Interscience, New York, 1984).
[5] $\rho_g = \lambda_g I_a / I_g$ $(g = a,b,c)$, where λ_g is the direction cosine between the symmetry axis of the top and the g inertial axis, I_a is the moment of inertia of the top about its symmetry axis, and I_g is a principal moment of the entire molecule. $F = \hbar^2/2rI_a$ is the reduced moment for the relative motion of the two groups, with $r = 1 - \Sigma_g \lambda_g^2 I_a / I_g$.
[6] Our value for $V_3(S_0)$ is in poor agreement with the $s - e/e - s$ energy difference for 1MN calculated by *ab initio* methods (10.2 kJ mol^{-1}) and with the barrier height determined by condensed phase NMR measurements (8.8–9.6 kJ mol^{-1}). See P. George *et al.*, J. Phys. Chem. **92**, 5656 (1988), and references therein.
[7] A. E. Dorigo, D. W. Pratt, and K. N. Houk, J. Am. Chem. Soc. **109**, 6591 (1987).
[8] G. T. Fraser, J. Chem. Phys. (in press), and references therein.
[9] See, for example, L. H. Spangler and D. W. Pratt, J. Chem. Phys. **84**, 4789 (1986); J. L. Tomer, L. H. Spangler, and D. W. Pratt, J. Am. Chem. Soc. **110**, 1615 (1988).

NOTES

A theoretical study of the dissociation energy of BH using quadratic configuration interaction

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The value for the dissociation energy (D_o) of the ground state of boron monohydride (BH) is given in the experimental compilation of Huber and Herzberg[1] (HH) as 3.42 eV (78.9 kcal mol^{-1}). This number is actually derived from an experimental predissociation limit in the electronic excitation spectrum to the lowest $^1\Pi$ state determined by Johns, Grimm, and Porter[2] to be $28\,850 \pm 150$ cm^{-1} (3.58 ± 0.02 eV or 82.6 ± 0.4 kcal mol^{-1}). This limit is interpreted as the energy required to reach the top of an outer repulsive hump in the $^1\Pi$ potential curve. A theoretical esti-