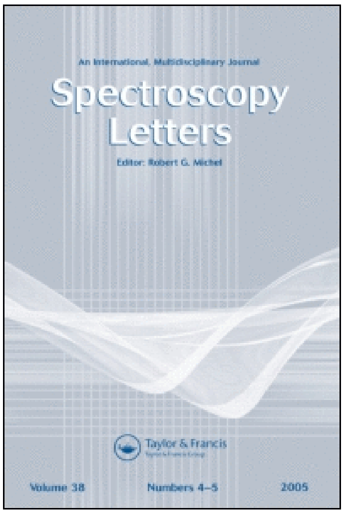

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Lowest Energy Singlet Transition in Biphenyl

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LOWEST ENERGY SINGLET TRANSITION IN BIPHENYL

Key words: biphenyl, electronic spectra, band fit, hidden band

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INTRODUCTION

The lowest energy band in the electronic absorption spectrum of biphenyl is broad and structureless. Considering a spectral comparison of biphenyl and related molecules, Platt[2] suggested that this band results from two different electronic transitions. Similarly, after making a fluorescence lifetime study, Berlman and Steingraber[3] predicted that the first singlet transition should be forbidden and thus the broad band should contain a hidden band. In this note we confirm this prediction.

MATERIALS AND METHODS

Biphenyl from Hopkins & Williams Ltd. was crystallized several times from methanol and was fractionally sublimed.

The absorption spectra were obtained with a Cary 17 spectrophotometer. Samples for determining the vapor spectra of biphenyl were vaporized directly in a 10 cm cylindrical quartz cell that was placed in the sample compartment of the instrument and was electrically heated. Fluorescence spectra were obtained by means of modular equipment consisting of a 1000 W Hanovia Xe-Hg lamp, a Hilger Monospek 1000 excitation monochromator, a Perkin-Elmer E-1 emission monochromator, an EMI 9558 QB photomultiplier tube, and the amplifier, recorder, wavelength drive and detector power supply from a Perkin-Elmer E-11 spectrophotometer.

RESULTS AND DISCUSSION

Spectra of biphenyl in solvents of different polarities and in the vapor phase were obtained at several temperatures in the range between 350 and 430 K. Solution spectra at all concentrations below the saturation point show no apparent sign of a hidden band at the low energy side of the main band. However, the vapor spectra show a shoulder around 270 nm. This observation agrees with a result reported by McLaughlin and Clark[4].

The vapor spectra were decomposed into two bands by the band fit method of Klabuhn, Spindler and Goetz[5]. The spectrum of biphenyl at 350 K gives $\bar{\nu}$ = 37,369 cm^{-1}, ε = 549 for band I and $\bar{\nu}$ = 42,179, ε = 14,410 for band II (FIG. 1). Since the concentration of biphenyl was unknown, the value of 14,410 for ε_{max} was obtained by extrapolation of values of molar absorptivities determined at higher temperatures by Almassy and Laemmel[6]. This value is consistent with that of a spectrum recently reported[4]. Band I is not a hot band since the ratio between intensities of bands I and II remains constant throughout the temperature range employed.

Berlman[7] predicted that the first singlet-singlet transition is $^1L_b \leftarrow {}^1A$ and that the second one should be $^1L_a \leftarrow {}^1A$. $^1L_b \leftarrow {}^1A$ transitions are polarized perpendicularly and $^1L_a \leftarrow {}^1A$ transitions are polarized along the axis of the molecule. Thus, if band I is assigned to $^1L_b \leftarrow {}^1A$ and band II to $^1L_a \leftarrow {}^1A$ transitions, an increase in the angle of twist between the rings should produce a smaller hypsochromic shift in band I than in band II. This assignment is supported by the spectra of highly twisted derivatives such as 2-methylbiphenyl and 2,2'-dimethylbiphenyl in which bands similar to band I are well resolved[8]. It is a well known fact that biphenyl in the vapor phase has a greater average angle of twist than that for biphenyl in solution[9], where as reported above, band I is partially hidden.

The absorption spectrum of biphenyl in cyclohexane shows a single band at 40,486 cm^{-1} with an ε_{max} value of 17,900. These values are attributed to band II since contribution of band I to the absorption maximum is negligible. The position of band I for solutions of biphenyl may be extrapolated from the relationship between twist angles and absorption maxima frequencies for different

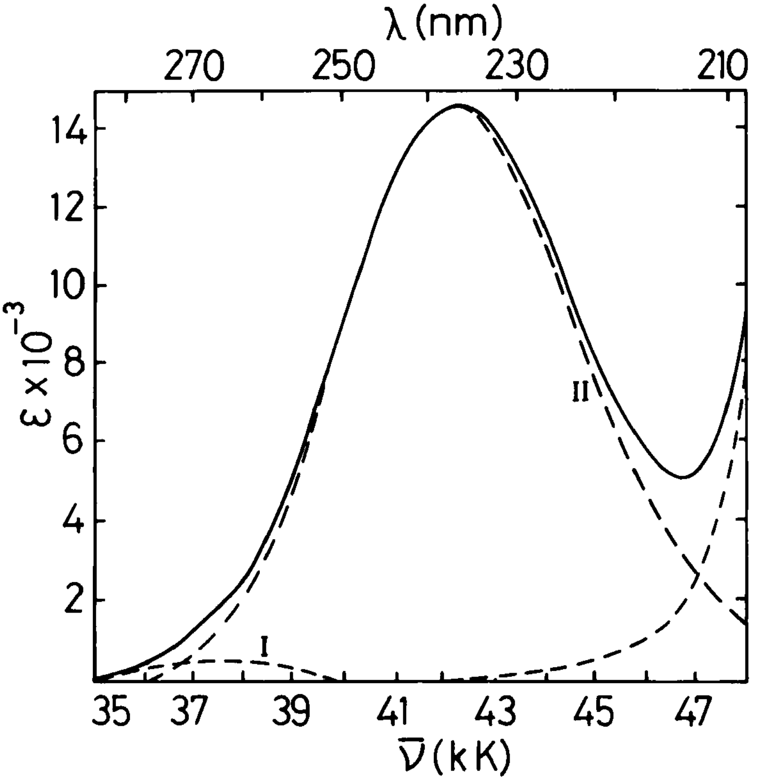

FIG. 1 Vapor absorption spectrum of biphenyl at 349 K (solid line) and bands fitted to it (dashed lines).

twisted derivatives. Using the values of 2-methylbiphenyl (58°; 35,765 cm^{-1}) and 2,2'-dimethylbiphenyl (70°; 38,023 cm^{-1}),[9] corrected for the inductive effect of the methyl groups taken as the difference between the $^1L_b \leftarrow {}^1A$ bands of benzene and toluene (1,056 cm^{-1}),[8] and using the twist angle of biphenyl as 23°,[9] we predict the frequency for the maximum of band I for biphenyl to be 35,088 cm^{-1}. Assuming that the ratio of intensities between bands I and II is the same in solution and in vapor, we find the ε_{max} of band I to be 682. This band should fall entirely under band II and thus should not be and is not apparent in the spectrum.

Band I corresponds to the first singlet-singlet transition and gives rise to a fluorescent state. The intrinsic lifetime of this state that was calculated by means of the Strickler and Berg[10] equation with our data for band I and the measured fluorescence spectra of biphenyl in cyclohexane, is 91.8 ns. This lifetime compares well with the experimental value[3] of 89.0 ns. On the other hand the lifetime calculated by Berlman[7] using the whole observed absorption band in the Strickler and Berg equation is 2.3 ns. The good agreement between our calculated lifetime and the experimental value, supports the validity of the assumption made and confirms the prediction of Berlman and Steingraber.

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