

Near-UV Spectra with Fully Resolved Rotational Structure of Naphthalene and Perdeuterated Naphthalene

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The combination of a single-frequency, tunable uv source with a well-collimated supersonic molecular beam and sensitive fluorescence detection has been used to obtain spectra with rovibronic resolution for some large organic molecules. The results of analysis of the 0_0^0 and 8_0^0 vibronic bands of the ${}^1B_{3u} \leftarrow {}^1A_g$ electronic transition for naphthalene and naphthalene- d_8 are presented. The obtained spectra are assigned using a rigid asymmetric rotor Hamiltonian and the structure in both the ground and electronically excited states is determined. The rotational temperature of the molecules cooled in the beam has been determined. The influence of the nuclear spin statistics on the line intensities is observed and discussed.

INTRODUCTION

Molecular spectroscopy, as a tool for the investigation of the structure of large molecules and their dynamic behavior, has experienced remarkable growth in the past few years. This growth was powered by the combination of three well-known techniques; single-frequency tunable lasers, supersonic beams, and sensitive fluorescence detection. The use of seeded molecular beams permits one to significantly reduce the linewidth due to Doppler broadening and the temperatures associated with vibrational and rotational motions. This not only simplifies the spectra considerably, but also makes possible a resolution which starts to approach that of ordinary microwave spectroscopy. The latter is practically limited to molecules with a permanent dipole moment, yet the optical or uv spectra can be obtained for every molecule. Further, when one performs an optical experiment, one can obtain information about molecules in electronically excited states in addition to the ground state. Additionally, the sensitivity of fluorescence detection applied in optical or uv regions surpasses the sensitivity of detection methods applied in other spectral regions. Finally, the use of seeded beams permits the study of weakly bound complexes of large molecules as well (1).

In spite of these advances, serious problems remain in the development of a truly general method of high-resolution linear laser spectroscopy for all molecules. Chief among these is the lack of a single-frequency tunable source in the ultraviolet, where most molecules have strong absorption bands. Suitable uv radiation can be produced by sum frequency mixing of single-frequency lasers (2) or by intracavity frequency doubling of single-frequency dye lasers (3, 4). The latter method is, in practice, simpler and most versatile.

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We have recently reported the development of a tunable, single-frequency uv source for high-resolution spectroscopy in the wavelength range 293–330 nm (4). In this paper we describe the results of experiments which were designed to demonstrate the applicability of this source to a "typical" problem in molecular spectroscopy. As test molecules naphthalene and perdeuterated naphthalene have been chosen. As a model of a large organic molecule naphthalene has played an important role in the history of spectroscopic and structural analysis. The first accurate structural measurements were done for a crystalline sample by X-ray analysis in 1950 (5). Radiative and nonradiative decay rates of electronically excited naphthalene in the low-pressure gas phase have been extensively measured (6–8). Under the same conditions the absorption spectra were recorded by Hollas and Thakur (9) in a 140-cm cell by means of a 3.4-m grating spectrograph, and carefully analyzed the barely resolved bands as rotational contours. They were able to determine rotational constants for ${}^1B_{3u}$ and 1A_g electronic states with surprisingly good accuracy by numerical simulation of those spectra. The spectra of naphthalene in the gas phase by Doppler-free, two-photon spectroscopy have been reported by Chen *et al.* (10). The resolution of 0.5 GHz was not sufficient to analyze the spectra. The same resolution can be achieved by application of supersonic free jet. This method allows to obtain single-photon fluorescence excitation spectra under collision-free conditions by simple means. Cold, free jet naphthalene spectra with distinct vibronic bands have been used for the latest vibrational assignments (11, 12). The logical extension of this experimental technique is reported here. By means of a highly collimated molecular beam and a single-frequency uv source of submegahertz spectral linewidth, one hundred times better resolution is achieved, which permits detailed structural analysis for the first time.

EXPERIMENTAL DETAILS

An overview of the experimental set up is presented in Fig. 1. The absorption spectra of naphthalene and perdeuterated naphthalene have been measured as excitation spectra by collecting the undispersed fluorescence.

A novel method of second harmonic generation (SHG) has been used in the development of our uv source, as described elsewhere (4). Briefly, as shown in Fig. 2, SHG is obtained by placing a LiIO_3 angle tuned single crystal of 1 mm thickness in a modified Spectra Physics ring dye laser. The doubling method is based on the fact that phase matching in a LiIO_3 crystal can be achieved by changing one angle only (ϑ) independent on the second angle (ϕ), as in the case of its analogs. Furthermore, LiIO_3 is less hygroscopic and insensitive for thermal detuning by residual absorption in the crystal.

In practice, the phase matching condition is fulfilled by a variation of two mechanical degrees of freedom of the Brewster positioned crystal. The first is a rotation around the normal to the crystal and the second is a slight change of the incidence angle of the fundamental wave around the Brewster angle. By this method phase matching can be achieved without disturbance of the linear polarization of the intracavity fundamental wave.

Stabilized scans over 120 GHz (4 cm^{-1}) with linewidths less than 0.5 MHz can easily be overlapped in order to obtain longer spectra. About 1 mW of cw power (at

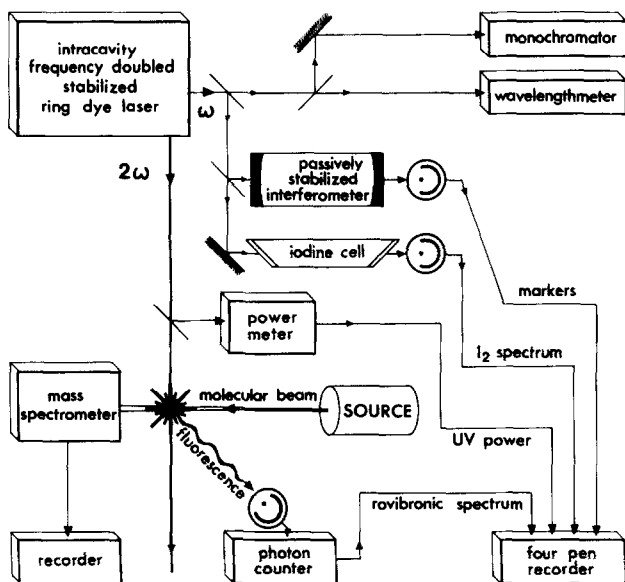


FIG. 1. Block diagram of the experimental set-up.

the interaction zone) has been applied to obtain the results reported in this paper. Reliable operation at 4 mW cw power is possible. Frequency calibration has been provided for the fundamental frequency of the dye laser. The absolute frequency has been monitored by 1-m Monospek monochromator, wavelength meter (13), and calibration absorption spectrum of iodine (14). We compared a number of absolute transition frequencies in iodine measured with our wavelength meter with a ± 40 MHz accuracy with those of the atlas (14). This showed that, in order to fully exploit the accuracy of the atlas, for an asymmetric transition the center of gravity of the observed absorption profile should be determined. In practice, this requires the cal-

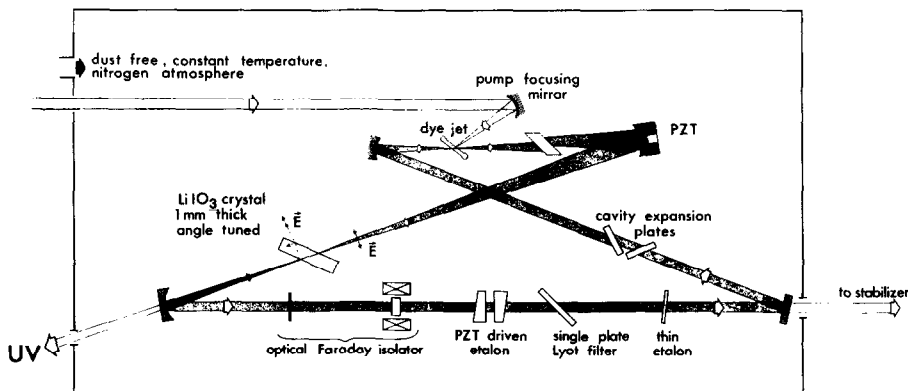


FIG. 2. The intracavity frequency doubled dye laser.

ibration spectrum to be digitized. In spite of this, the iodine cell is the simplest and most versatile frequency monitor for tunable lasers working in the green-to-red part of the spectrum. The relative frequency has been measured by a sealed off, temperature stabilized, confocal Fabry-Perot interferometer with 299.32 MHz free spectral range (fundamental).

The molecular beams were formed by expanding noble gases (He and Ar) through a nozzle with a small admixture of the molecules to be studied. In order to achieve rotational resolution the molecular beam was strongly collimated by two skimmers with a two-step differential pumping system. This multichamber molecular beam machine is described in more detail in Ref. (13). The intensity and composition of the argon seeded molecular beam has been monitored by a quadrupole mass spectrometer. The interaction zone where the laser beam crossed the molecular beam has been placed 30 cm from the nozzle orifice in the chamber with pressure kept below 2×10^{-6} Torr. This chamber was separated by the buffer chamber from the source chamber where the pressure below 10^{-3} Torr has been maintained. The skimmers between chambers separated by 150 mm were of 0.75 and 3 mm diameter. The arrangement of the source made of quartz is presented in Fig. 3. This kind of source construction is simple and has many convenient features. The mounting on flexible bellows assures easy positioning of the nozzle against the first skimmer. The quartz construction allows heating up to 550°C , while the sample can be observed through a transparent flange. The main advantage of this construction is the ability to load a crystalline or liquid sample while the beam machine is kept under vacuum. After

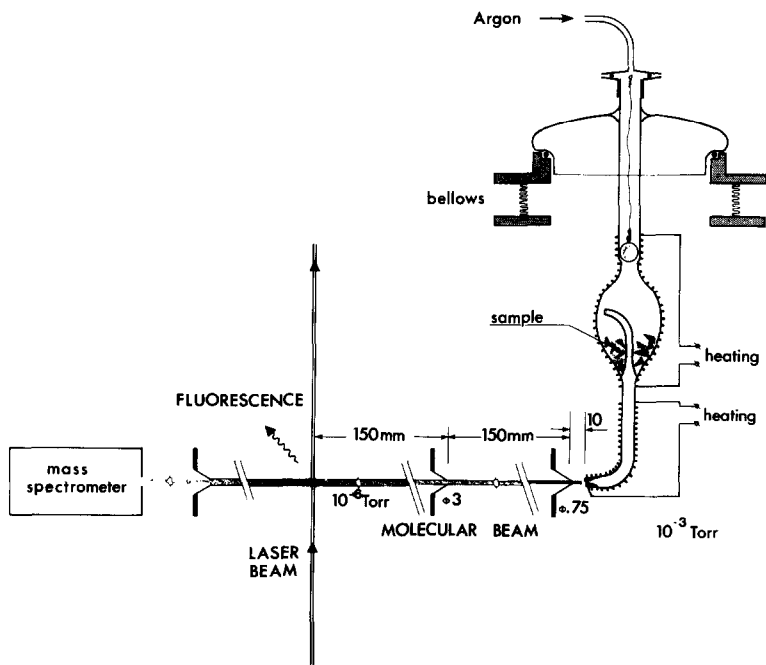


FIG. 3. The construction of the source and schematic view of the molecular beam.

the loading, the quartz ball with a small slit is placed above the container in order to prevent a back flow of vapors of the investigated molecule. The nozzle of 100 μm diameter has been positioned about 10 mm from the first skimmer. Two heating wires wrapped around the container and nozzle pipe assured their independent temperature which was monitored by two thermocouples. A source temperature of 105°C was chosen, while the nozzle was kept slightly hotter. The temperature of the container determined the vapor pressure of naphthalene, a total backing pressure of argon of 7 bars was chosen. A flux of 8×10^{12} naphthalene molecules per second was estimated in the interaction zone.

The uv beam was focused at the crossing point with the molecular beam. The very elongated waist (1 m length and 0.5 mm diameter) of the uv beam crossed the molecular beam perpendicularly with an accuracy of a few arc minutes. In order to avoid stray light the fused silica windows were placed at the Brewster angle and separated about 60 cm from the interaction zone. The set of diaphragms along the entering and outgoing beams was further optimized to diminish the stray light. The total amount of stray light was kept about 1000 counts per second per milliwatt of laser power.

Relatively strong spectra were obtained when fluorescent light was collected with 5% efficiency by a primitive fused-silica two-lens system. In this case a residual Doppler linewidth of 35 MHz is mainly determined by the divergence of the molecular beam. The data reported here were obtained with a resolution which was high enough to completely resolve the rotational structure of naphthalene. The improved fluorescence collection system is presented in Fig. 4. The overall collection efficiency of this system is in the order of 25%. The spatial filtering features of this optics allows one to reduce the stray light and to obtain linewidths below 10 MHz. With such a resolution very strong spectra of deuterated pyrazines were measured.

The image of the fluorescing spot at the interaction zone was focused by optics at the 9-mm-diameter photocathode of the EMI 9863/350 QA photomultiplier. The refrigerated photomultiplier tube housing (TE 104TS-RF, Products for Research Inc.) reduced the dark counts to less than 10 counts per second. The excited uv fluorescence signal was monitored by an Ortec Brookdeal 5C1 photon counter with 0.2 sec integration time and recorded by a four-pen recorder simultaneously with the iodine absorption spectrum and frequency markers at the fundamental frequency of the dye laser. A small fraction of the uv beam was sent to a Molelectron power meter and was recorded by the fourth channel of the recorder. The data acquisition by the recorder is the major drawback of the set-up. The slow rise-time of the recorder (0.35 sec) determines the scan speed of the laser. At least 1 sec was needed to reproduce a line shape of 35 MHz FWHM. Thus, the fastest admissible scan of the laser was about 120 GHz/hr. During such a long period of time the frequency marking interferometer drifts thermally, causing a relative frequency error of 10^{-3} (1 MHz uncertainty per 1 GHz of frequency scan). Fast storage of data in a digital memory can significantly improve the accuracy of measurements, since the obtained spectra are strong enough to be recorded with a scan speed of 60 GHz/min. Even a passively stabilized interferometer should be sufficiently stable to maintain the relative frequency calibration of 5×10^{-5} for 1 or 2 min which would result in a similar accuracy of rotational constants obtained from the spectrum.

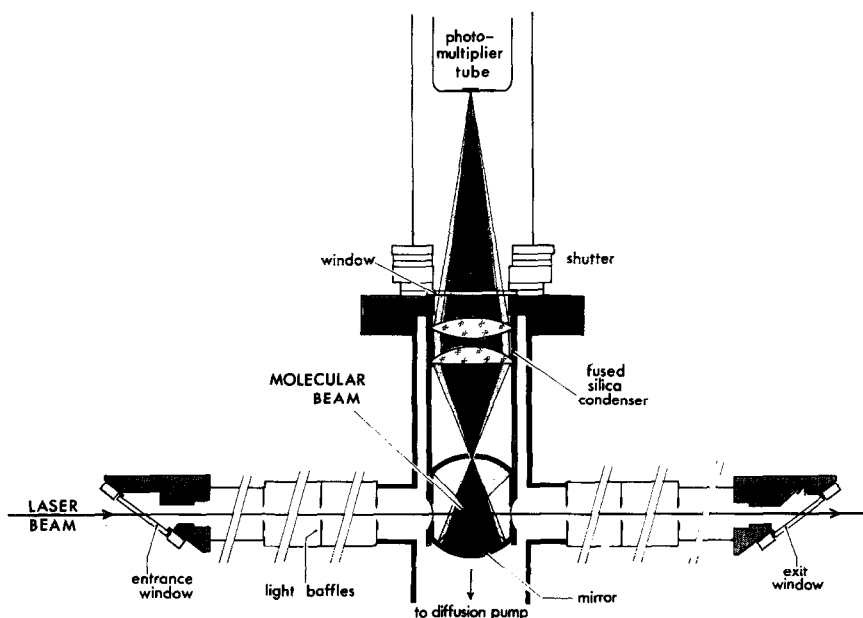


FIG. 4. The optical part of the molecular beam machine. The collecting mirrors are spherical, both with radii of 35 mm. The upper mirror with a 3.8-mm hole also serves as a spatial filter. The residual reflection from the Brewster positioned exit window is trapped in the absorption cone.

RESULTS

The assignment of vibronic bands of the $S_2/S_1 \leftarrow S_0$, $\pi\pi^*$ electronic transitions for naphthalene and naphthalene- d_8 is well known (9, 11, 12). However, the notation is often confusing since the choice of coordinate axes follows at least two conventions. In this paper the rotational structure of a - and b -type transitions was investigated for both normal and perdeuterated naphthalene. The 0_0^0 and $\bar{8}_0^1$ vibronic bands of the $S_1 \leftarrow S_0$, $\pi\pi^*$ electronic transitions were chosen as examples. Our nomenclature follows Ref. (11), where the bar over the mode number denotes b_{1g} symmetry of the vibrations. The rotational coordinates are presented in Fig. 5.

A typical vibronic band extended over 120 GHz and consisted of a few hundred well-resolved rotational lines. Every line of every spectrum measured was uniquely assigned with the help of an asymmetric rotor program described in Ref. (15). The central part of 40–50 GHz containing 200–300 lines alone was enough to fully assign the rovibronic spectrum. The S/N ratio varied from 10 to 1000 for various spectra recorded with 1–2 mW uv power and integration time 0.2 sec. The weakest spectra recorded were 0_0^0 transitions of naphthalene and naphthalene- d_8 . The strongest spectra obtained with a S/N ratio of 1000 were those obtained with collecting optics shown in Fig. 4.

The labeling of rovibronic lines is based on J'' , J' , K''_{-1} , K'_1 , and K'_{-1} quantum numbers. The prime sign denotes the excited state and the double prime the ground state. Generally the notation is of the ${}^{\Delta K-1}\Delta J_{K''_{-1}, K'_1}(J'')$ type, similar to that described by Herzberg (6). A typical recording of the rotational structure of a relatively weak

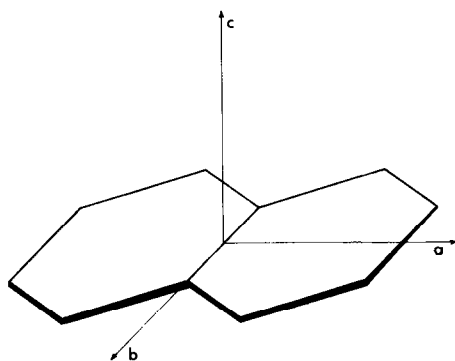


FIG. 5. The skeleton of the naphthalene molecule. The origin of the rotational coordinate system is at the centre of mass.

parallel a -type 0_0^0 vibronic transition (at ${}^1B_{3u} \leftarrow {}^1A_g$ electronic origin) was already shown in Fig. 3 of Ref. (4).

Figure 6 presents an example of a perpendicular b -type ($\Delta K_{-1} = \pm 1$) band. This transition follows the selection rules: $ee \leftrightarrow oo$ and $oe \leftrightarrow eo$ for $K''_{-1}K''_1 \leftrightarrow K'_{-1}K'_1$. The construction from subbands of the central part of the $\bar{8}_0^1$ vibronic band of naphthalene is shown. The lower two tracks represent the actual fluorescence excitation spectrum and frequency markers. The b -type transition has almost no characteristic features and is built up from complicated subbands. The assignment has been simplified by the rotational constants which are known accurately from the a -type parallel transition.

The $\bar{8}_0^1$ transition is strong, which allows us to investigate how the configuration of hydrogen spins influence the intensity of separate rovibronic lines. The intensity of single rovibronic transitions is described by

$$I = I_0 g_{J''K''_{-1}K''_1} A_{J''K''_{-1}K''_1} e^{-hE(J''K''_{-1})/kT_{rot}}, \quad (1)$$

where I_0 is a constant and A_{JK} are Hönl-London factors for a given transition. Since naphthalene is a near prolate symmetric top, the Hönl-London factors are taken for the boundary case of the symmetric top molecule (17). The $g_{JK_{-1}K_1}$ coefficient denotes the statistical weight of the lower state.

For the separate J'' , K''_{-1} , K''_1 state

$$g_{J''K''_{-1}K''_1} = (2J'' + 1)g_n,$$

where g_n is the statistical weight of the nuclear spin. The value of g_n is determined by the number of spin configurations allowed for a given rovibronic eigenstate in the ground electronic level. In the case of the 1A_g state of naphthalene, $g_n = 76$ for the states with K_{-1} and K_1 both even; $g_n = 60$ for all the remaining states.

For some of the subbands presented in Fig. 6 the alternating intensity of lines below and above a smooth, dashed envelope is clearly visible. The intensity ratio for these lines is in quite good agreement with these considerations. The analysis of line intensities, by means of formula (1), permits the determination of the rotational temperature of naphthalene under our experimental conditions. The temperature determined from the spectrum presented in Fig. 6 is 2.1 ± 0.3 K. The rotational

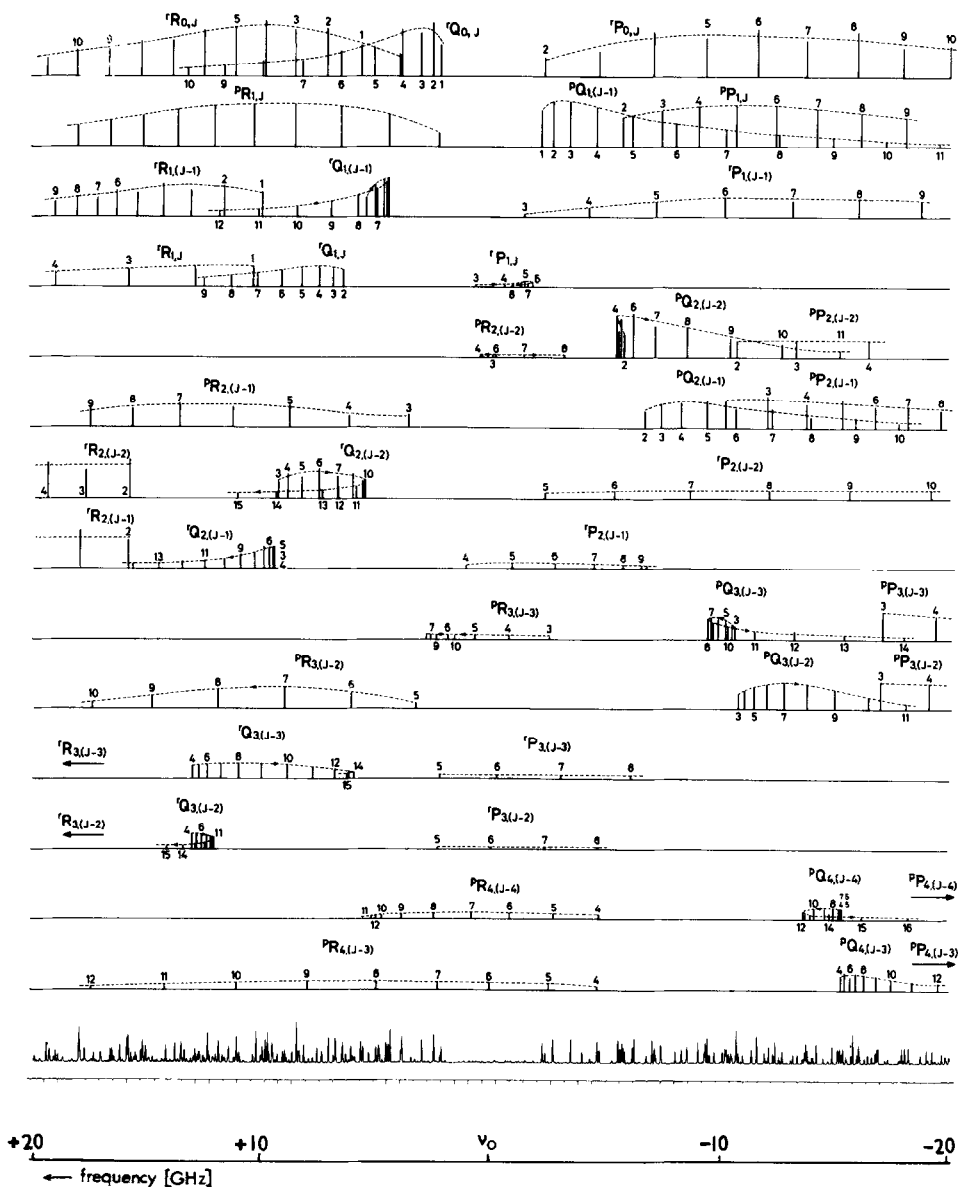


FIG. 6. The b -type, $\bar{8}_0^1$ vibronic band of naphthalene constructed from subbands. The first track above the frequency axis is the actual recording of this band with frequency markers every 598.64 MHz. Only the central 40 GHz are presented.

temperature determined from the 0_0^0 vibronic transition is, within the error, in agreement with this value. The determination of T_{rot} from a rotationally resolved spectrum is simpler than obtained from band contour analysis (18, 11).

The lifetime of the excited rovibronic molecular eigenstates can be determined

from the line broadening. Unfortunately the spectra have only been measured with 35 MHz resolution. This value of the residual Doppler broadening allows only for the statement that the lifetime of all the measured transitions is longer than 5 nsec. To evaluate the literature values ranging from 200 to 450 nsec [for example (6)], submegahertz resolution is needed. The results of our measurements are summarized in Table I. This table contains rotational constants for ground and excited states calculated from the two different types of transitions. The central frequencies and planarity defect are also included.

The statistical errors in the rotational constants obtained from the fit of each individual vibronic band are within the last digit of the values given in Table I.

The comparison of rotational constants for the ground state obtained from *a*- and *b*-type transitions given in Table I shows the actual inaccuracy of our measurements. Although the statistical relative error (the standard deviation), calculated from the self consistence of the spectrum, never exceeds 10^{-4} , the uncertainty of the results presented is much larger. The total error is dominated by two errors. At first the relative inaccuracy in the distance of our frequency markers (FSR) is 2×10^{-4} . The other systematic error is caused by thermal drift of the frequency markers during the scan. This drift has only a slight reflection in the self consistence of the spectrum.

TABLE I

Molecular Constants of Naphthalene and Perdeuterated Naphthalene in their 1A_g and ${}^1B_{3u}$ electronic states ($\Delta A = A' - A''$, $\Delta B = B' - B''$, and $\Delta C = C' - C''$, $\Delta I = I_c - I_b - I_a$)

state	constant	naphthalene		naphthalene-d ₈	
		a-type	b-type	a-type	b-type
${}^1A_g, 0^0$	A'' (MHz)	3105.1	3108.8	2517.5	2614.1
	B'' (MHz)	1231.4	1228.8	1094.8	1093.4
	C'' (MHz)	883.9	881.0	772.2	771.1
	ΔI (amu·Å ²)	-1.4	-0.2	-0.2	-0.2
${}^1B_{3u}, 0^0$	ΔA (MHz)	-77.51		-59.96	
	ΔB (MHz)	-17.82		-16.45	
	ΔC (MHz)	-15.22		-13.33	
	ΔI (amu·Å ²)	-1.6		-0.3	
	ν_0 (cm ⁻¹)	32018.583 (5)		32136.670 (5)	
${}^1B_{3u}, \bar{8}^1$	ΔA (MHz)		-74.55		-58.36
	ΔB (MHz)		-18.72		-16.50
	ΔC (MHz)		-16.50		-13.54
	ΔI (amu·Å ²)		0.4		0.0
	ν_0 (cm ⁻¹)		32453.522 (5)		32556.048 (5)

However, it can be observed directly by review scans done at higher speed. In this way we were able to avoid relative errors larger than 10^{-3} and this is the final accuracy of the rotational constants given in Table I. Generally, the data obtained from *b*-type spectra are more reliable because of larger *S/N* ratio and better self-consistence. In spite of an accuracy of only 10^{-3} , the data in Table I are much more accurate than any reported before [(11, 9, 12) and references therein]. Tribute must be paid to Hollas and Thakur, who were able to calculate rotational constants by band contour analysis and simulation of the vapor cell spectra (9). Their results deviate only by about 1% from those in Table I, obtained from spectra with a thousand times better resolution.

CONCLUSIONS

The molecular structure of naphthalene can be precisely determined by measurements of spectra for various nuclear substitutions. Without nuclear substitution, one can still conclude from the small planarity defects that naphthalene is planar in its ground and excited states. Unfortunately, our accuracy does not allow for investigation of zero-point, out of plane motion of hydrogen and deuterium atoms.

UV linear spectroscopy with rovibronic resolution proved to be useful and can become a routine method for precise structural analysis of relatively large molecules. The versatility of the method can be improved by extension of the existing uv single-frequency sources and use of versatile and fast data acquisition electronics. The latter is necessary, since high resolution, dynamics of line intensities, and complexity of the vibronic bands result in spectra with an information capacity of an order of several megabits. The uncertainty of rotational constants can be reduced to below 10^{-6} by the application of a more-accurate frequency calibration than the one we used. Using standard laboratory techniques a resolution of 1 MHz can be achieved. For many molecules this will allow the determination of their lifetime in excited states by lineshape analysis.

The set-up described has also been used for the study of Van der Waals clusters (1). The hyperfine and spin-rotation structures of small molecules (with collimated thermal beam) (19) and interesting spectra of the molecular eigenstates of so-called "intermediate level structure" molecules (20, 21) were also investigated by means of the experimental method presented here in detail. These results will be described in detail elsewhere.

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