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Spectral assignment of dual conformers of 1,2,3,6,7,8-hexahdropyrene in the supersonic jet

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The laser-induced fluorescence excitation (FE) spectra of 1,2,3,6,7,8-hexahdropyrene has been observed in jet-cooled condition. The FE spectrum show the existence of interconvertible conformers, chair and boat, with 0–0 bands 12 cm^{-1} apart. On the basis of semiempirical calculations and single vibronic level luminescence, the longest wavelength band at $30\,653\text{ cm}^{-1}$ has been ascribed to chair conformer and the one at $30\,665\text{ cm}^{-1}$ to the boat conformer. The low-frequency vibronic bands have been tentatively assigned. The lifetimes of low-frequency vibronic levels follow the trend reported by Jacobson *et al.* [J. Chem. Phys. **87**, 269 (1987)] for naphthalene monoderivatives, namely, they fluctuate at low excess energies, but merge and decrease steadily at high energies of excitation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1329998]

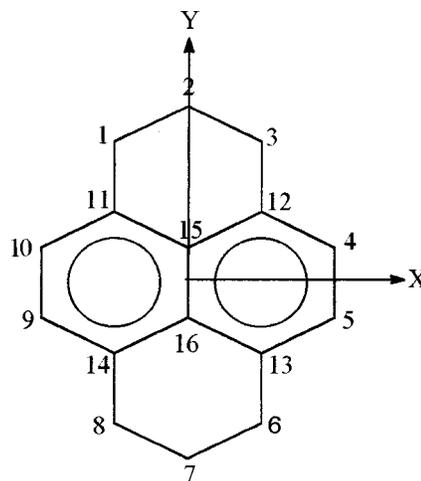
I. INTRODUCTION

Geometrical conformers have received the attention of chemists from almost the start of pursuit of organic chemistry. If the barrier between the conformers is high, each individual conformer is stable and can be investigated individually (after isolation) by chemical, nuclear magnetic resonance (NMR),^{1(a)} and other techniques. If the barrier is low and the thermal passage rate is appreciable, one gets a mixture of dynamically interconvertible conformers. Although separation might still be possible in some cases by lowering the temperature, in general one has to obtain information about interconverting conformers by *in situ* studies of the mixture. NMR has played a great role in spectroscopically determining the nature of such interconverting conformers. If the barrier is such that the frequency of passage between the two forms is less than the difference in NMR spectral frequency of two forms, then each conformer leaves its own fingerprint. If not, the spectrum corresponds to the average structure. Whether a resolved or an average spectrum is obtained depends on the temperature and the barrier height. A rule of thumb is that if the barrier is much lower than 10 kcal/mol, then the fingerprinting of individual conformers cannot be obtained by the required lowering of temperature, because the solidification of the matrix disturbs, after a point, the dynamic equilibrium between the possible conformers. Barrier height up to a minimum of 6 kcal/mol has been determined by extending the NMR studies up to 90 K.^{1(b)} Cold matrices have sometimes been used to isolate the energetically unfavorable form, but then the question of matrix modification remains.

The best way of studying interconverting conformers is in cold supersonic jet, where the organic molecule has been vaporized, mixed with inert carrier gas such as helium or argon and expanded through a small orifice into vacuum

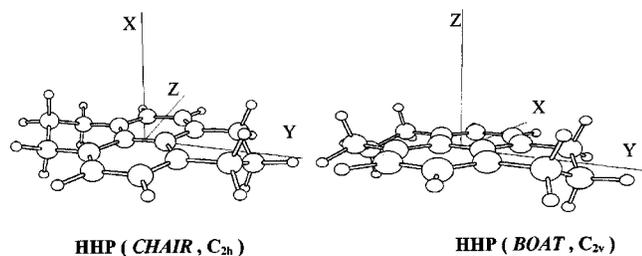
from a high pressure. The low temperature and the isolation of molecules in seeded supersonic jet prevent interconversion between conformers—at least, not fast enough to blur the characteristic optical frequencies of the two conformers. Such *in situ* fluorescence and ionization studies have been reported for inequivalent and equivalent conformers. *p*-dihydroxybenzene,² 1,2-dimethylnaphthalene (DMN),³ 2-vinylnaphthalene,⁴ 2-methoxynaphthalene⁵ are a few examples of the inequivalent case while equivalent conformers are observed for 9,10-dihydroanthracene (DHA),⁶ 9,10-dihydrophenanthrene (DHP),⁷ methyl naphthalenes,⁸ octafluoronaphthalene (OFN),⁹ etc.

Previously, we reported tunneling between two equivalent conformers of DHA (Ref. 6) and DHP (Ref. 7) and discussed jet spectra of molecules with possible puckering in side chains. We have chosen here 1,2,3,6,7,8-hexahdropyrene (HHP) for our study, which can exist in a number of configurations. There are two equivalent chair and two equivalent boat configurations, the mirror image pairs being of identical energy



HHP (PLANAR, D_{2h})

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The chromophore is the naphthalene unit, which is one of the most favorite molecule for spectroscopy in molecular beams, mainly due to its high symmetry, conveniently accessible electronic transitions, long fluorescence lifetimes and high vapor pressure. The parent naphthalene and its different derivatives mainly obtained by attaching different functional groups like F,¹⁰ OH,¹¹ CN,¹² NH₂,¹³ CH₃,⁸ COOH,¹⁴ OCH₃,⁵ etc. have been used to explore torsion, inversion, and isomerization. HHP may be considered as a naphthalene derivative where two (CH₂)₃ chains are attached symmetrically to the naphthalene moiety. HHP and naphthalene are close to each other in symmetry. Indeed, if we take the planar form of HHP, the molecule HHP belongs to the same D_{2h} group as naphthalene. Comparison of the spectra of HHP with that of naphthalene may therefore be interesting. Two conformers, boat and chair, seem possible—the former belonging to C_{2v} and the latter to C_{2h} group. The two forms, boat and chair, ought to be very close in total energy and spectral frequencies, because the difference in energy can only arise out of long-distance through-bond and through-space interactions. We thought it interesting to compare the boat form, where the two perturbers (i.e., the two CH₂ groups raised above/below the molecular plane) are on one side of the molecular plane and made the two π lobes (of positive and negative phase) inequivalent with respect to reflection in the naphthalene plane, with the chair form which maintains the overall equivalence of the two antiphase π lobes above and below the molecular plane. One might anticipate a difference in selection rules due to difference in symmetry of the two conformers, which may be handy in the spectral identification of the conformers.

II. EXPERIMENT

The compound HHP obtained from Aldrich is of 99% purity. The details of supersonic jet experimental set-up is described elsewhere.⁶ In brief, the sample was heated to about 140 °C to increase sample vapor pressure and then expanded with argon as carrier gas into a vacuum chamber through a 0.5 mm diam orifice of a pulsed nozzle valve (General Valve Corp.) with a frequency of about 10 Hz. The background pressure of the chamber during the experiment was maintained at about 4×10^{-5} Torr by the operation of a 6 in. oil diffusion pump (Varian) backed by a mechanical rotary pump. The output of the Dye laser (PDL 3), pumped by a Nd:YAG laser (Quanta Ray DCR-11) is frequency doubled by a KDP crystal and intensity check is maintained by Autotracker III (INRAD). The second harmonic output crossed the jet at about 15 mm downstream of the nozzle orifice. The laser induced fluorescence was collected perpendicular to both the laser and the jet directions. The signal was

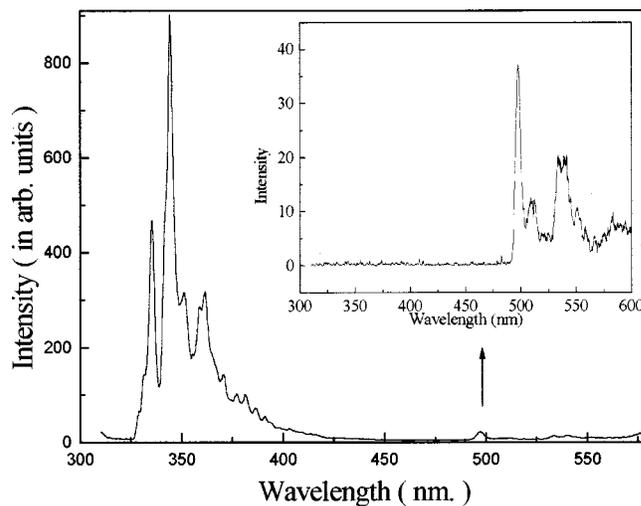


FIG. 1. Fluorescence emission spectrum of HHP in methyl cyclohexane at 77 K. (Inset) Phosphorescence spectrum.

detected by an EMI-9781 R photomultiplier after passing through an optical filter to eliminate the scattered laser light, amplified in a current amplifier and then averaged by a Boxcar Integrator (PAR model -64). The normalized output from the Boxcar was then recorded in a PC. Dispersed fluorescence spectra of selected single vibronic levels were recorded with a 20 in. monochromator (Jobin Yvon); the resolution was better than 25 cm^{-1} . The time resolved studies were done by recording undispersed fluorescence from a selected vibronic level in a digital storage oscilloscope (Tektronix TDS-350).

III. RESULTS AND DISCUSSION

A. Spectra of HHP in condensed phase

The low-temperature (77 K) fluorescence spectrum and the phosphorescence spectrum of HHP in methylcyclohexane glass are shown in Fig. 1. Since, the condensed phase spectra are too broad, we shall not discuss these further, except drawing attention to following features of the spectra.

(a) The spectra of HHP are less resolved than that of naphthalene. This is understandable from consideration of symmetry and vibronic level density. Although, the symmetry of planar-HHP is same as that of naphthalene, boat or chair forms have lower symmetries which make the selection rules less restrictive for HHP. In addition, there should be a number of additional low-frequency methylene vibrations in HHP which are absent in naphthalene. These cause overlap of transitions leading to less-resolved spectra.

(b) The lifetime of the phosphorescence is 45 ms while that of naphthalene is much longer.¹⁵ The lifetime of the phosphorescence is controlled by the spin-orbit coupling matrix which might couple the three T_1 states to the ground state if their total symmetries are the same. In boat (C_{2v}) and chair (C_{2h}) forms the three triplet states are, respectively, of total symmetry A_2 , A_1 , and B_2 in group C_{2v} and B_u , B_u ,

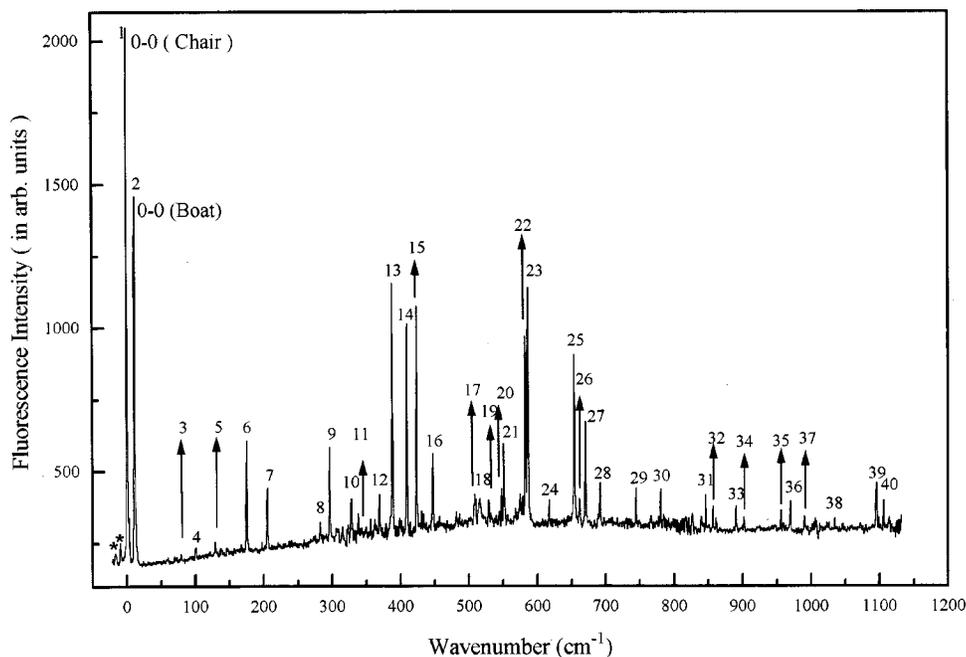


FIG. 2. Fluorescence excitation spectra of HHP in the supersonic jet seeded in He.

and A_u in group C_{2h} while the ground state symmetry is A_1 in both cases. One of the triplet components of the boat form, therefore, has the same total symmetry as the ground singlet state and may be the doorway level for leaking to the ground state. In naphthalene itself, like the *c*-HHP, there is no such state and hence, its lifetime gets longer. Still another explanation of the shorter lifetime may be provided in terms of the density of state. The density of states is higher in HHP compared to naphthalene and hence has faster radiationless transition than naphthalene.

(c) The lifetime of fluorescence from the S_1 state is also shorter (about 18 ns) for HHP than that of naphthalene (~ 99 ns),¹⁶ but it is of the same order as 1,4,5,8, tetramethyl naphthalene (~ 22 ns).¹⁶ Again, this may be expected from considerations of the spin-orbit coupling matrix element and the density of states.

B. 0_0^0 bands in the jet spectrum

On the long wavelength side of the fluorescence excitation spectrum there appears two bands ~ 12 cm^{-1} apart (30653 cm^{-1} and 30665 cm^{-1}) at Fig. 2. For ascertaining whether the two peaks are originating from two bands of the same species or two different ones, we resorted to the intensity saturation technique prescribed by Levy *et al.*¹⁷ The intensities of the two bands varied at the same rate with change in laser intensity, which is consistent with the conformer hypothesis. We tried the NMR technique at room and low temperatures to find out whether the two forms leave their characteristic imprints or not. In any of the two forms, boat or chair, the two H atoms attached to C_2 or C_7 should have different chemical shift. However, the NMR spectrum indicates a planar form, average of the boat and chair forms—even at temperatures as low as 160 K. This indicates that the interconvertible rates are higher than the difference in NMR frequencies of the two H atoms and that the barrier between the two forms could be considerably less than 10 kcal/mol.

However, there are no features in the vibronic spectrum which might lead one to suspect tunnelling between two conformers separated by very low barrier height. We, therefore, ascribe the two bands to two 0–0 bands corresponding to boat and chair forms with a barrier large enough for preventing tunnel splitting, but low enough for interconversion²³ in the NMR time scale. Two important questions immediately crop up from this assignment, one regarding frequency and the other regarding intensity. First, what causes naphthalene, B-HHP, and C-HHP to differ in frequency and which of the two bands is to be ascribed to the boat form and which to the chair form? Second, why are the two 0–0 bands of both boat and chair forms much stronger (relative to the vibronic manifold) compared to that of naphthalene of approximately the same symmetry?

To answer some of the questions we have taken recourse to theoretical calculations. Geometry optimization by *ab initio* calculations on such a large molecule proved beyond the capacity of our computational machinery. We, therefore, optimized the ground state geometry for both chair and boat forms by semiempirical AM1 Hamiltonian through MOPAC (version 5.0). The total energy of the molecule has been optimized using Davidson–Fletcher–Powell method. For more precise and accurate measure of optimized energy we have gone over to configuration interaction calculations involving 1500 configurations, which is the maximum number allowed in our computational program. Care is taken so that gradient remains below 0.001. The potential energy curve (PEC) with reference to variation of the z -coordinate (out-of-plane) of the C_7 atom for both S_0 and S_1 states are shown in Fig. 3. While the ground state energies are obtained by keeping the C_7 z -coordinate fixed and allowing the rest of the atoms to search for global minima, the excited state potential energy curve is obtained by adding simply the vertical transition energy to the energy of each optimized ground state geometry keeping the C_7 z -coordinate (measured in Å) fixed. The

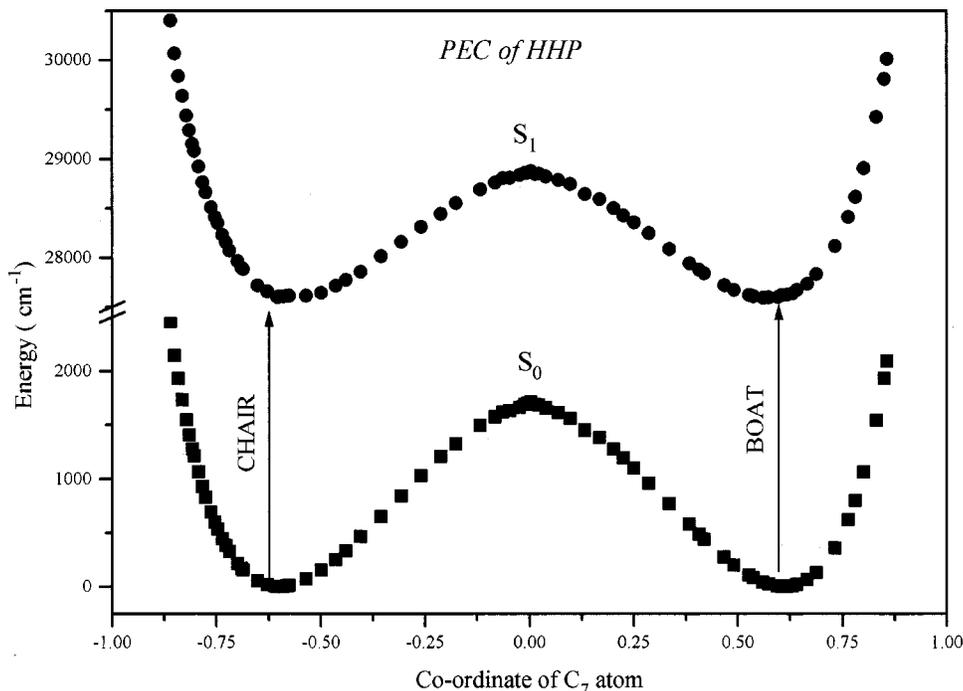


FIG. 3. Potential energy curve (PEC) of HHP with respect to the out-of-plane movement of the C_2 atom.

calculated points fit well a curve simulated by assuming a potential expression,

$$V(z) = a_1 z + a_2 z^2 + a_3 z^3 + a_4 z^4,$$

the values of the constants a_1 , a_2 , a_3 , and a_4 [when $V(z)$ is measured in cm^{-1}] being, respectively, 101, -9800 , -250 , and 12 000 for the S_0 state and 88, -8200 , -345 , and 11 000 for the S_1 state.

In the minimum energy configuration in both the conformers, out-of-plane C_2 and C_7 atoms are seen to make an angle of about 27° with the planar naphthalene moiety. The calculated ground state energies at minima show consistently that boat and chair forms are almost equal in energy. In view of the smallness of the calculated energy difference, the semiempirical calculations (AM1, MM2) were repeated starting from different initial geometries, but each time the energies at optimized geometry indicated $2\text{--}6\text{ cm}^{-1}$ more stability for the boat form. An *ab initio* GAUSSIAN 98 calculation using 6-31G** as basis set was then carried out for the optimized geometry. The boat was found to be stabler by 8 cm^{-1} . However, the calculated higher stability of the boat form is so small that we decided not to rely on this small number. Perhaps, of greater significance is the experimental fact that in the crystalline state the chair form is the preferred form,¹⁸ although there is always the possibility of reversal of stability of the two forms on going from the solid state to the vapor state. A more extensive *ab initio* study of the isolated molecule (and packed set of molecules) is required. A qualitative perturbative model which deals directly with the energy difference between the two forms, rather than calculate the energies of the two forms individually, might be a desirable approach. From the point of view of through-space dipole-dipole interaction, the orientation of the two end dipoles located near C_2 and C_7 should provide slightly more stability to the chair form. The different components of the

through-bond interactions, on the other hand, are not easy to decipher in this way. One can only speculate. In the boat form, the two H atoms attached to C_2 and C_7 atoms are on one side of the molecular plane, while in the chair form these are on the opposite sides of the molecular plane. If we associate a net positive charge on H-atoms, p -orbitals of C_{15} and C_{16} atoms should be drawn out to the same side of the molecular plane. In contrast, in the chair form p -orbitals of C_{15} and C_{16} atoms are drawn on opposite sides of the naphthalene plane. As a result the repulsion between the filled p -orbitals of C_{15} and C_{16} atoms could be more for the boat form than for the chair form, thereby stabilizing the latter.

The barrier between the two forms is found to be about 1686 cm^{-1} ($\sim 4.7\text{ kcal/mol}$) in the ground S_0 state, but about 1200 cm^{-1} in the S_1 state. These values are qualitatively consistent with our NMR and jet spectrum.²³ This reduction in barrier height on excitation is in agreement with observations on other similar molecules investigated in this laboratory, such as DHA (Ref. 6) and xanthene (Ref. 19) where the two conformers are distinguished by the sign of the puckering coordinate. In the S_1 state, the calculated barrier for HHP is much too high to allow tunnel splitting in puckering vibration—at least, not at low energies in excess of the 0–0. The barrier height for simultaneously flipping of both carbon atoms, in converting one boat to another equivalent boat conformer or from one chair to another chair form is about 3386 cm^{-1} ($\sim 9.7\text{ kcal/mol}$), nearly double that for converting the chair to the boat form.

The average 0–0 frequency of B-HHP and C-HHP may be compared with that of naphthalene.²⁰ On methylation, at position 1 of the naphthalene, the 0–0 band is red shifted by 246 cm^{-1} with respect to the parent naphthalene. In the case of 1,8-DMN (Ref. 21) this redshift with respect to naphthalene is about 2 times this value. In the case of HHP the

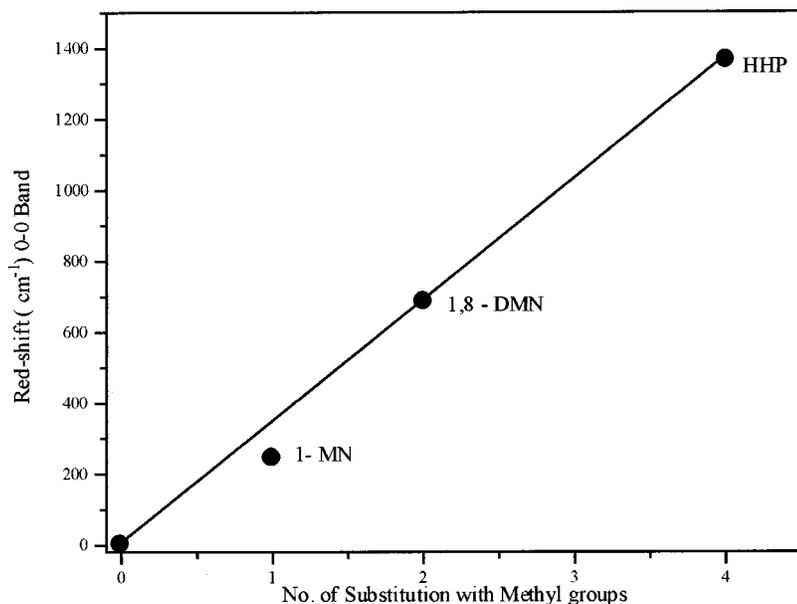


FIG. 4. Redshift (cm^{-1}) of the origin band of naphthalene with increasing number of methyl substituents.

observed red shift of 1366 cm^{-1} which is twice that of DMN. This implies that the perturbations in energies at 1, 4, 5, 8 positions of naphthalene are roughly additive. Figure 4 shows the plot of 0-0 frequency against the number of substituents in x -position.

The intensities of the 0-0 bands of HHP may be contrasted with that of naphthalene.²⁰ The intensity of the 0-0 band of both conformers is much higher compared to that of the parent chromophore, naphthalene. In the case of naphthalene the first electronic transition is long axis polarized. Though the $S_1 \leftarrow S_0$ [${}^1B_{3u} \leftarrow {}^1A_g$] transition is not a symmetry forbidden one, the configuration interaction between the two lowest $\pi\pi^*$ Huckel configurations of the same symmetry occur in such a way that its transition moment nearly vanishes $\{f=0.001\}$.²⁰ The state S_3 is also of ${}^1B_{3u}$ symmetry, where the two transition moments add up to give an intense band $\{f\sim 2\}$. The ratio in which the two configurations mix in the S_1 state of naphthalene derivatives depends on the symmetry of the substituted derivatives as well as on the nature of the substituents. In 1- or 2-substituted naphthalenes, the fragile accidental cancellation is lost leading to an intense 0-0 band compared to the short axis polarized vibronic bands which derive their intensities mainly from the $S_0 \rightarrow S_2$ (${}^1B_{2u} \leftarrow {}^1A_g$) transition. It is pertinent to find out whether the accidental cancellation of $S_1 \leftarrow S_0$ transition moments occurs even in derivatives which have the same or nearly the same symmetry. To answer this question we previously studied OFN,⁹ and found that the 0-0 band was intense. But in that case, the nature of the substituent is so different that it could influence the mixing process of two configurations. In the present case of HHP, not only the approximate symmetry of the compound is the same as that of naphthalene, but the substituents are also of the same carbon family. We find that even in HHP, the ratio of the two coefficients gets changed from that in naphthalene, which makes the oscillator strength four times larger in HHP than in naphthalene.

We noted a significant difference in intensities of the

two 0-0 bands corresponding to two different forms. Since, our quantum mechanical calculations of $S_0 \rightarrow S_1$ transition probabilities of boat and chair forms generated nearly the same number, the difference in radiative transition probability is obviously not the explanation for the observation. Also, the calculated barrier between the two forms is 1686 cm^{-1} , while the energy difference between the two forms is of the order of a few cm^{-1} . It is improbable, therefore, that the observed 30% difference in peak height has been caused by a population difference at the time of molecules settling down in one of the two wells. Still another explanation for the relative 0-0 intensity could be that the Franck-Condon (FC) factors for 0-0 transitions are different for the two forms. However, our calculated FC factors are the same for the two forms. We, therefore, think that the difference in nonradiative rates to the $T_1 \rightarrow S_0$ states is responsible for the difference in the lifetimes of the two S_1 ($v=0$) states or the difference in the two 0-0 peak heights.

C. Vibronic bands

Figure 2 shows that intense 0-0 bands are followed by weak vibronic bands up to about 350 cm^{-1} higher in energy; beyond 350 cm^{-1} vibronic bands of relatively higher intensities appear. In order to understand the vibronic features we have calculated the S_0 vibrational frequencies for the two conformers using MOPAC-AM1 and HYPERCHEM 5.0 AM1 packages. The same frequencies are obtained from the two packages. S_1 frequencies are also calculated by MOPAC-AM1-CI method, but these are considered to be much less reliable, specially if the vibration contains significant contributions from chromophoric modes. Table I shows the various vibrational modes, their symmetry designations in D_{2h} , C_{2h} , and C_{2v} corresponding to hypothetical planar HHP or naphthalenic core, chair HHP and boat HHP, respectively, and the frequencies of the two stable forms. It may be noticed that, differences between corresponding S_0 and S_1 frequencies, or that between corresponding frequencies of the two conform-

TABLE I. Calculated vibrational frequencies (cm^{-1}) of HHP and corresponding symmetries.

Serial No.	Boat (C_{2v})			Chair (C_{2h})			(D_{2h}) Sym.	Comments
	S_0	S_1^a	Sym.	S_0	S_1^a	Sym.		
1	78	73	$1A_2$	78	72	$1A_u$	A_u	Out-of-plane
2	89	84	$1A_1$	89	84	$1B_u$	B_{1u}	Do
3	120	115	$1B_1$	120	112	$1B_g$	B_{2g}	Do
4	181	170	$2A_1$	183	168	$2B_u$	B_{1u}	Do
5	199	193	$1B_2$	196	192	$1A_g$	B_{3g}	Do
6	259	256	$3A_1$	262	257	$3B_u$	B_{1u}	Do
7	319	269	$2A_2$	315	265	$2A_u$	A_u	Do
8	325	290	$2B_2$	325	290	$2A_g$	B_{3g}	Do
9	355	352	$2B_1$	365	356	$3A_u$	B_{3u}	Essentially in-plane
10 ^b	423	416	$4A_1$	422	415	$3A_g$	A_g^b	In-plane symmetric elongation
11	442	443	$3B_2$	447	461	$4A_g$	B_{3g}	In-plane
12 ^b	447	446	$3A_2$	428	417	$2B_g$	B_{1g}^b	Asymmetric rocking
13	488	451	$3B_1$	509	486	$3B_g$	B_{2g}	In-plane
14	503	510	$4B_2$	486	485	$4B_u$	B_{2u}	Do
15	517	513	$4A_2$	530	516	$4A_u$	A_u	Do
16	566	551	$5A_1$	598	580	$5B_u$	B_{1u}	Do
17	570	553	$4B_1$	541	522	$4B_g$	B_{2g}	Do
18	608	587	$5A_2$	616	597	$5A_u$	A_u	Do
19	620	609	$5B_2$	602	601	$5A_g$	B_{3g}	Do
20	707	663	$6A_1$	699	655	$6B_u$	B_{1u}	Do
21 ^b	747	746	$7A_1$	746	747	$6A_g$	A_g^b	In-plane (breathing)
22	782	778	$6B_2$	791	787	$7B_u$	B_{2u}	In-plane
23 ^b	782	776	$6A_2$	780	776	$5B_g$	B_{1g}^b	In-plane (asymmetric)
24	839	820	$7B_2$	834	812	$7A_g$	B_{3g}	In-plane
25	849	832	$5B_1$	851	836	$6B_g$	B_{2g}	Do
26	870	849	$8A_1$	872	853	$8B_u$	B_{1u}	Do
27	906	890	$7A_2$	903	885	$6A_u$	A_u	Do
28 ^b	912	904	$9A_1$	911	903	$8A_g$	A_g^b	Do
29	918	913	$8B_2$	918	914	$9B_u$	B_{2u}	Do
30	925	915	$6B_1$	926	918	$7B_g$	B_{2g}	Do
31	975	961	$9B_2$	976	963	$9A_g$	B_{3g}	Do
32	981	971	$8A_2$	981	969	$7A_u$	A_u	Do
33	1030	1031	$10B_2$	1030	1032	$10B_u$	B_{2u}	Do
34	1052	1049	$10A_1$	1052	1050	$10A_g$	A_g^b	Do
35	1083	1076	$11B_2$	1083	1074	$11B_u$	B_{2u}	Do
36	1086	1080	$7B_1$	1086	1076	$8A_u$	B_{3u}	Do
37 ^b	1115	1104	$11A_1$	1115	1106	$11A_g$	A_g^b	Do
38	1128	1120	$9A_2$	1127	1117	$8B_g$	B_{1g}^b	Do
39	1129	1122	$12B_2$	1130	1125	$12B_u$	B_{2u}	Do
40	1133	1127	$8B_1$	1134	1127	$9A_u$	B_{3u}	Do

^aThe S_1 frequencies are obtained by MOPAC using the AM1 Hamiltonian. These are not reliable figures as one can see in the naphthalene itself. These frequencies were therefore appropriately normalized for naphthalenic core vibrations.

^bNaphthalenic modes.

ers are not large. The same is true for the normal mode description of the two conformers. The normal modes of the two conformers were matched not only by frequencies but also by comparing simultaneously the symmetry of the dynamics of two vibrations in two windows, using the program HYPERCHEM 5.0. The symmetry of any two corresponding vibrations in the two conformer may be supposed to be derived from a symmetry representation of the parent D_{2h} group by appropriate symmetry-lowering perturbations. For example, the $A_1 (C_{2v})$ representation for the boat form and the $A_g (C_{2h})$ representation for the chair form can be derived from the parent $A_g (D_{2h})$ representation; however, $A_2 (C_{2v})$

representation and $A_g (C_{2h})$ representation cannot be derived by reduction of symmetry from any representation of the D_{2h} group, and hence, these cannot be considered as corresponding vibrations.²² We have cross-checked that the symmetries of the two corresponding vibrations of the two conformers are consistent with the symmetry of naphthalenic core vibrations from which these are derived, by symmetry reduction.²²

The observed bands have been assigned as shown in Table II. The following comments are pertinent as regards the assignment of bands:

(a) In the fluorescence excitation (FE) spectrum of the chromophore (i.e., naphthalene) itself, the intense vibronic

TABLE II. Frequencies (cm^{-1}) and lifetimes (ns) obtained from the FE spectra and time-resolved studies and their corresponding assignments.

Band No.	Obs. frequencies (relative to band 1) (intensity)	Assignment	Lifetimes (ns)
1	0 (s)	$0_0^0(C)$	115
2	12 (s)	$0_0^0(B)$	85
3	78(vvw)	$0_0^0(B) + \nu_1(66)$	
4	99 (vw)	$0_0^0(B) + \nu_2(87)$	82
5	128 (vw)	$0_0^0(C) + \nu_3'(128)$	96
6	175 (w)	$0_0^0(B) + \nu_4(163)$	83
7	205 (w)	$0_0^0(C) + \nu_5'(205)$	112
8	282 (vw)	$0_0^0(B) + \nu_6(270)$	
9	296 (w)	$0_0^0(B) + \nu_7(284)$	88
10	328 (vw)	$0_0^0(C) + \nu_8'(328)$	88
11	339(vvw)	$0_0^0(C) + \nu_3' + \nu_5'$	
12	369 (w)	$0_0^0(B) + \nu_1 + \nu_7$	105
13 ^a	387 (s)	$0_0^0(C) + \nu_{10}'(387)$	105
14 ^a	409 (s)	$0_0^0(B) + \nu_{10}(397)$	72
15 ^a	423 (s)	$0_0^0(C) + \nu_{12}'(423)$	105
16 ^a	447 (w)	$0_0^0(B) + \nu_{12}(435)$	75
17	509 (vw)		
18	515 (vw)		
19	528 (vw)		
20	547 (vw)		
21	550 (w)		103
22 ^a	581 (s)	$0_0^0(C) + \nu_{21}'(581)$	105
23 ^a	586 (s)	$0_0^0(B) + \nu_{21}(574)$	87
24	617 (vw)		65
25 ^a	653 (s)	$0_0^0(C) + \nu_{23}'(653)$	85
26	661 (vw)		
27 ^a	670 (mw)	$0_0^0(B) + \nu_{23}(658)$	61
28	691 (vw)		63
29 ^a	744 (vw)	$0_0^0(C) + \nu_{28}'(744)$	64
30 ^a	780 (vw)	$0_0^0(C) + \nu_{28}(768)$	
31	846 (vw)		
32	857 (vw)		
33	890 (vw)		72
34	902 (vw)		
35	955 (vw)		
36	969 (vw)		
37	989(vvw)		
38	1034(vvw)		
39	1095 (w)		84
40	1106 (w)		

^aNaphthalenic vibrations allowed in both conformers. ν' refers to vibration frequency of the chair form; ν to that of the boat form.

bands have been thoroughly studied and appropriately assigned by others.²⁰ The a_g and b_{1g} in-plane modes appear strongly, some of the observed S_1 frequencies being $435(b_{1g})$, $501(a_g)$, $702(a_g)$, $908(b_{1g})$, and $987(a_g)$. Since, the approximate symmetry of the immediate environment of the chromophoric unit within HHP is same as that of the free chromophore (i.e., naphthalene), the same naphthalenic vibrations may be expected to be coupled with the $S_0 \rightarrow S_1$ electronic transition of HHP. These should appear as pairs with comparable intensities for both conformers and are therefore comparatively easily recognizable. The mechanism by which the vibrational bands derive intensities could be somewhat different from that of the parent naphthalene of nearly the same symmetry. As stated before, in the naphthalene molecule there occurs accidental cancellation of transition moments due to configurational mixing, and hence the

pure electronic 0–0 band has little to offer to the intensities of the vibronic bands, which are essentially short-axis polarized due to mixing with the $S_2(^1B_{2u})$ state (Herzberg–Teller mechanism). In the case of HHP, however, 0–0 bands of conformers are strong and hence are capable of lending intensity to vibronic bands through the Franck–Condon mechanism. Thus, the vibronic bands of HHP, depending on their symmetries, can borrow intensity from either the 0–0 band of the $S_0 \rightarrow S_1$ transition in which case it will be long axis polarized, or the $S_0 \rightarrow S_2$ transition, in which case it will be in-plane short axis polarized. Both types, $a_g(D_{2h})$ and $b_{1g}(D_{2h})$ of vibration should appear in the jet-FE spectrum. In our assignment we have assumed that all symmetry modes that permit out-of-plane polarization by borrowing intensity from $\sigma \rightarrow \pi^*$ transition do not appear strongly in the $\pi - \pi^*$ transition.

Table I shows that there are some frequencies which are forbidden in both the conformers, some are forbidden in one conformer but allowed in the other, and some are allowed in both the conformers. Vibrations belonging to the last group are essentially naphthalenic vibrations; these are indicated by * in Table I. The following naphthalenic vibrations (S_0) appear in Table I: $\nu_{10}(\sim 423 \text{ cm}^{-1})$, $\nu_{12}(438 \{\text{average}\} \text{ cm}^{-1})$, $\nu_{21}(\sim 746 \text{ cm}^{-1})$, $\nu_{23}(\sim 781 \text{ cm}^{-1})$, $\nu_{28}(\sim 911 \text{ cm}^{-1})$, $\nu_{34}(\sim 1052 \text{ cm}^{-1})$, $\nu_{37}(\sim 1115 \text{ cm}^{-1})$, and $\nu_{38}(\sim 1128 \text{ cm}^{-1})$. However, in view of the unreliability of calculations of S_1 frequencies by the AM1 method, these frequencies need calibration before being compared with the observed FE spectrum. The calibration has been done by extending the AM1 calculations to the naphthalene molecule as well. For each vibrational frequency of naphthalene, the calibration factor needed for correspondence between the calculated frequency and the observed frequency²⁰ was found out. For example, for $8b_{1g}$ (i.e., lowest b_{1g}) frequency of naphthalene the AM1 calculated one is 547 cm^{-1} while the observed value from the FE spectrum is 435 cm^{-1} in the S_1 state and hence the calibration factor is around 0.8. The lowest b_{1g} frequency of HHP is multiplied by 0.8 before comparison with experimental frequencies. Thus the calculated calibrated frequencies for $\nu_{10}(a_g)$, $\nu_{12}(b_{1g})$, $\nu_{21}(a_g)$, $\nu_{23}(b_{1g})$, $\nu_{28}(a_g)$ of HHP are 384 cm^{-1} , 358 cm^{-1} , 549 cm^{-1} , 734 cm^{-1} , 767 cm^{-1} , respectively. Indeed, in the FE spectrum we find four relatively intense bands at 387 cm^{-1} , 409 cm^{-1} , 423 cm^{-1} , and 447 cm^{-1} ; these are assigned to $\nu_{10}(a_g)$ and $\nu_{12}(b_{1g})$ modes superposed on 0–0 transitions of both boat and chair forms. These presumably correspond to observed 435 cm^{-1} (b_{1g}) and 501 cm^{-1} (a_g) frequencies (S_1) of naphthalene. The next strong doublet in the HHP (FE) spectrum occurs at $\sim 584 \text{ cm}^{-1}$. These are assigned to ν_{21} superposed on the two 0–0 bands. It corresponds to the observed naphthalene vibronic (a_g) transition at 702 cm^{-1} . The next naphthalenic vibronic transitions in HHP are observed at $\sim 661 \text{ cm}^{-1}$ and $\sim 762 \text{ cm}^{-1}$. These are assigned to ν_{23} and $\nu_{28}(a_g)$ and correspond to $7b_{1g}(908 \text{ cm}^{-1})$ and $7a_g(987 \text{ cm}^{-1})$ of naphthalene.

Apparently, the frequencies of naphthalenic modes have changed to a considerable extent from the free chromophore. Although the chain linked at 1, 4, 5, and 8 positions might have introduced stiffness into the vibrations of ring atoms

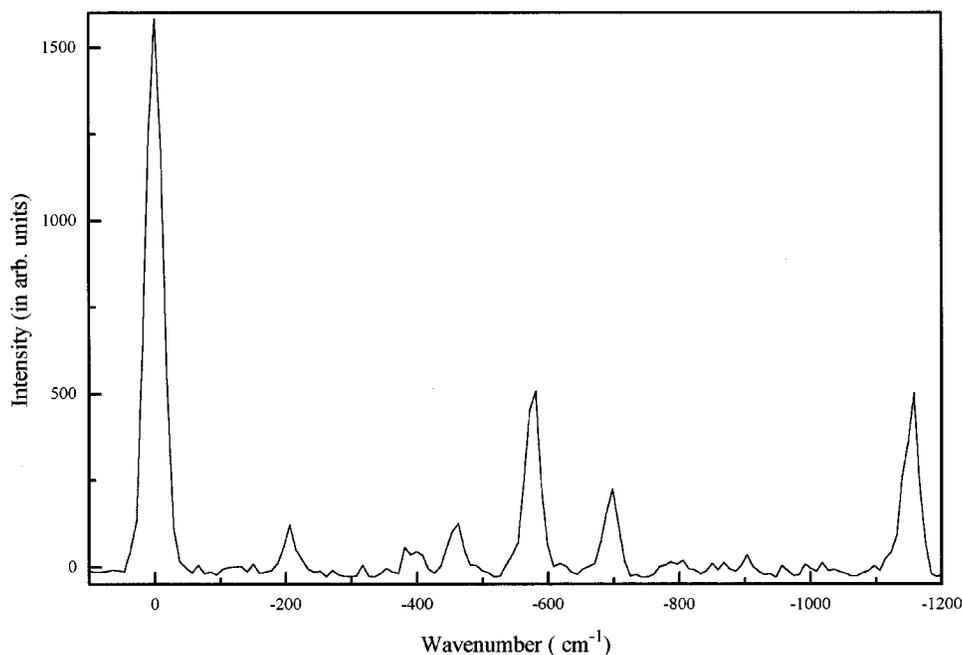


FIG. 5. SVL-1, dispersed emission spectra of HHP when excited at 0_0^0 (C) ($30\,653\text{ cm}^{-1}$).

leading to an upward shift, it seems that the reduction in frequency due to attachment of heavier mass at the four positions of HHP have more than compensated the increase, caused by the stiffness.

(b) The appearance of low-frequency modes below 350 cm^{-1} in the FE spectra of HHP is somewhat surprising and needs to be discussed separately. These frequencies do not appear in the spectra of naphthalene or 1-methylnaphthalene^{8(c)} or acenaphthene.²¹ In 1,8-dimethylnaphthalene²¹ two weak bands appear at 33 cm^{-1} and 88 cm^{-1} intervals from the 0–0 band, but these have been assigned to methyl rotations. In 2-methylnaphthalene^{8(c)} spectrum and the 0–0 SVL is lost; these have been ascribed to extensive mixing of the ground

state modes in the S_1 excited state, because of reduction in symmetry. The spectral features of HHP resembles more that of the β -derivatives of naphthalene more than that of the α -derivatives, namely, it has a relatively strong 0–0 band and weak vibronic activity in low-frequency regions. No marked mirror-symmetry breakdown between the FE spectrum and the 0–0 SVL (Figs. 5 and 6) is noted in HHP. This is understandable, because in HHP-conformers the reduction of symmetry of the immediate chromophoric environment over that of the free chromophore is very little, and hence, extensive mixing of S_0 normal modes in the excited S_1 state does not occur.

The low-frequency out-of-plane vibrations (ν_1 to ν_8) of HHP are combinations of methylenic chain modes and out-

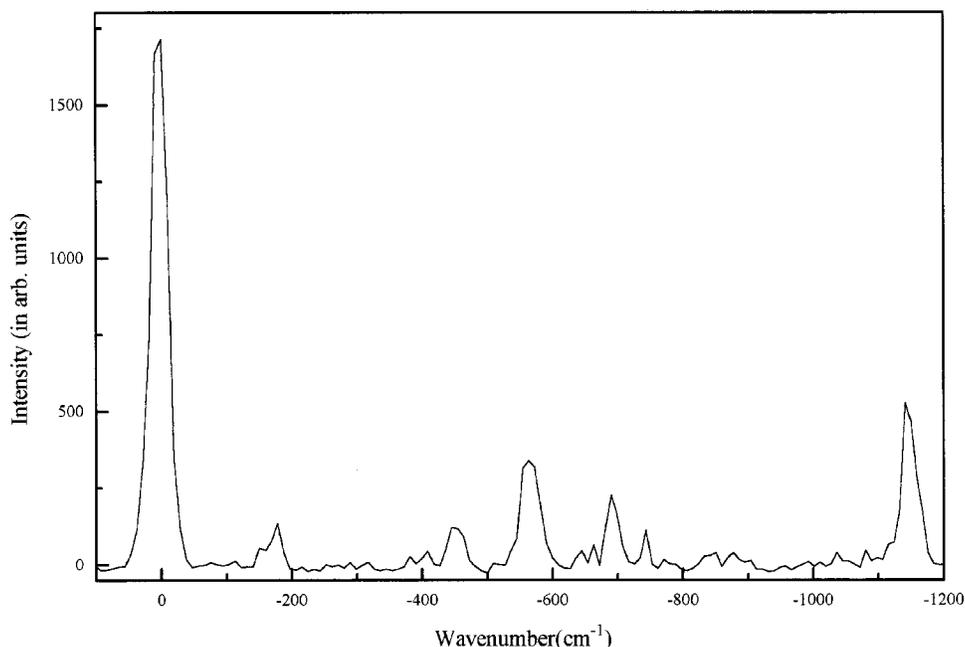


FIG. 6. SVL-2, dispersed emission spectra of HHP when excited at 0_0^0 (B) ($30\,665\text{ cm}^{-1}$).

of-plane ring modes. The symmetry of the mixing ring modes are such that these vibronic bands do not appear in the FE spectrum of naphthalene (D_{2h}) and hence can not be compared with. These, however, get selectively allowed in one conformer or the other because of loss of planarity and/or loss of two C_2 axes of symmetry and thus serve as signatures for the conformers. In contrast to naphthalenic modes which appear in pairs, these vibrations appear singly. In the chair form of C_{2h} symmetry, for example, u -vibronic bands are absent throughout the spectrum. The detailed mechanism of intensity borrowing by the allowed vibronic transitions in the two conformers is complicated. However, it may be generally expected that the coupling with an electronic transition of the chromophoric ring should depend upon the relative amplitudes of ring vibrations vis-à-vis methylenic modes, as long as we are dealing with a symmetry allowed transition of a conformer. We have calculated the ratios of the sum of the squares of displacement amplitudes of ring atoms to that of all atoms for the first eight out-of-plane vibrations. These ratios of amplitude factors (A) are shown in Fig. 7 and compared with the experimentally obtained intensities of the first eight vibronic bands. Considering the simplicity of our assumption, the agreement between the two bar diagrams is good.

D. SVL spectra

The SVLs of the two bands (1 and 2) have the general features expected for 0-0 bands, namely a strong 0-0 emission followed by relatively weak vibronic activity (Fig. 5). This confirms our assignment of the two bands at $30\,653\text{ cm}^{-1}$ and $30\,665\text{ cm}^{-1}$ to 0-0 bands of the two conformers. The SVLs are of much lower resolution compared to that of the FE spectrum. However, these have the advantage of selective excitation of conformers, and do therefore, provide

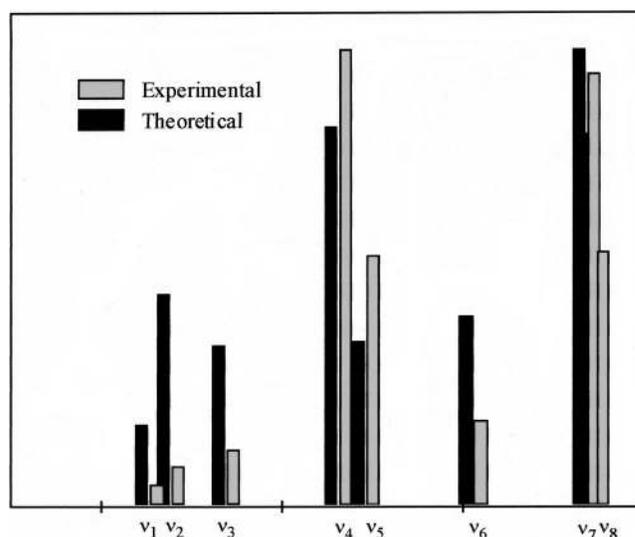


FIG. 7. Comparison of experimental and theoretical values of relative weights of ring modes in vibronic bands (see text).

luminescence spectra of pure conformers. The low-frequency vibronic bands of the SVL spectra carry the signatures of the symmetries of the two conformers. As, already discussed, each of the frequencies ν_1 to ν_8 is allowed only in one conformer or the other, but not in both, and thus should be useful in identification of the conformers. Unfortunately, most of the low-frequency vibronic bands of the SVL are too weak for analysis. However, the band around 200 cm^{-1} with reasonable intensities in both SVL and FE spectra is of significance in recognizing the conformer. Table I shows that the modes which are relevant for discussing the vibronic features at the 200 cm^{-1} region are 4 and 5. The semiempirical calculations which are more reliable more for the S_0 state

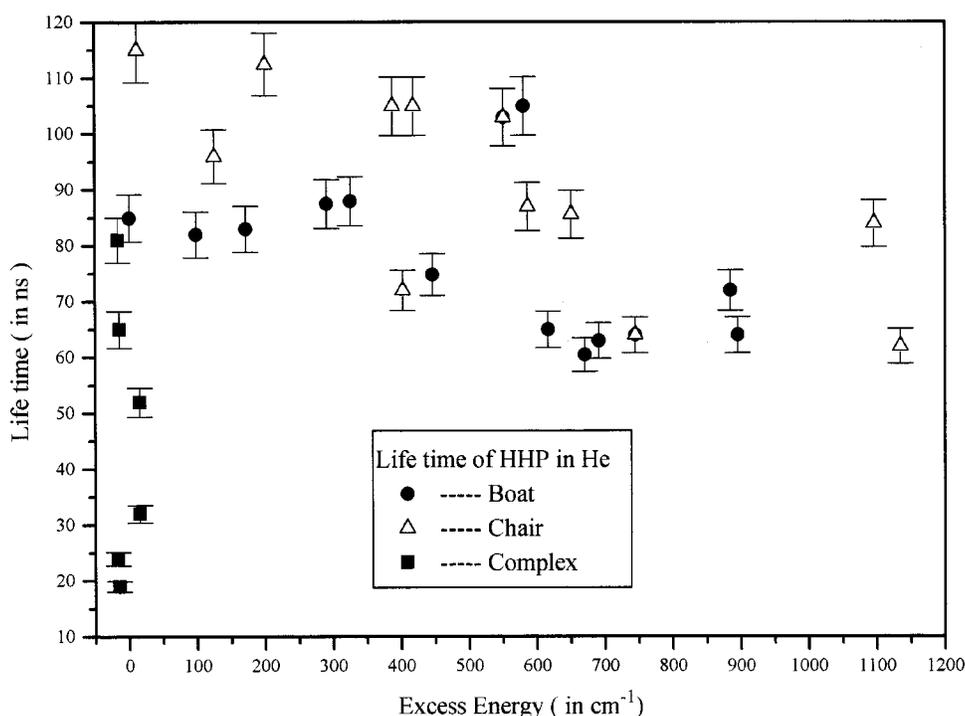


FIG. 8. Variation of lifetime of HHP with excess energy above the origin transition.

than the S_1 state, reveals that each of the two modes has almost matched frequencies for the two conformers, but the selection rules are distinctly different. The ν_4 vibronic band ($\sim 182\text{ cm}^{-1}$) is allowed in the boat conformer, while the ν_5 vibronic band ($\sim 198\text{ cm}^{-1}$) is allowed for the chair form. Out of the two SVL's, SVL-1 (Fig. 5) on excitation at $30\,653\text{ cm}^{-1}$ contains a vibronic band at 205 cm^{-1} , while the SVL-2 (Fig. 6) on excitation at $30\,665\text{ cm}^{-1}$ contains a band at $\sim 178\text{ cm}^{-1}$. Thus, SVL-1 has to be assigned to the chair form and the SVL-2 to the boat form. This means that the longer wavelength band of the 0–0 doublets of the FE spectrum has to be assigned to the chair form. This conclusion based on symmetry restrictions seems to be more robust than the previous inconclusive arguments based on calculated small numbers. The details of SVLs of other bands will be discussed elsewhere.

The naphthalenic vibrations should appear at nearly the same frequencies in the SVL's of the two conformers. Table I shows that the naphthalenic vibrations are $\nu_{10}, \nu_{12}, \nu_{21}, \nu_{23}, \nu_{28}, \nu_{34}, \nu_{37}, \nu_{38}$. As already discussed, these frequencies need to be calibrated by comparing AM-1 frequencies with the experimental S_0 vibrations for naphthalene itself.²⁰ The calibrated theoretical values for $\nu_{10}, \nu_{12}, \nu_{21}, \nu_{23}$, and ν_{28} , for HHP are $394\text{ cm}^{-1}, 415\text{ cm}^{-1}, 595\text{ cm}^{-1}, 758\text{ cm}^{-1}$, and 792 cm^{-1} , respectively. Experimentally, we observe naphthalenic bands at $\nu_{10}(\sim 403\text{ cm}^{-1}), \nu_{12}(\sim 458\text{ cm}^{-1}), \nu_{21}(\sim 572\text{ cm}^{-1}), \nu_{23}(\sim 694\text{ cm}^{-1})$, and $\nu_{28}(\sim 770\text{ cm}^{-1})$. The decrease in frequency from that of the parent naphthalenic chromophore has already been discussed earlier.

E. Lifetimes of emission

The lifetimes of the 0th and vibronic levels of the S_1 state of naphthalene derivatives have been investigated by Rice *et al.*^{8(b)} The general observation is that near the 0th level lifetimes fluctuate considerably, being characteristic of the nature of the vibronic state. At high energies, however, the lifetimes become only a function of excess energy. On the basis of a number of approximations they obtained k_{nr} 's of vibronic states and found that k_{nr} increases with excess energy until saturation is reached. The explanation offered is as follows: k_{nr} depends both on the coupling matrix element as well as on the density of states. When the density of states is low, the matrix element, which is sensitive to the nature of the state, is important. But, when density of states is large the matrix element is some sort of average and k_{nr} increases with density of states which increases with excess energy. Our experimental results on lifetimes (Fig. 8) follow the same general trend as reported by Rice and co-workers; lifetimes fluctuating strongly for both conformers at small excess energies, then decreases at large excess energies. However, we expected the onset of steady decrease and merging of lifetimes to begin at an excess energy smaller than that for the monoderivative of naphthalene, because the density of states in HHP at a definite excess energy ought to be higher for HHP which has a large number of low-frequency vibrations. This does not seem to be the case. This could be due to the high symmetry of HHP compared to naphthalene monoderivatives. A similar effect is observable in naphthalene

itself—the fluctuation continues for excess energy larger than the limit set by the 1-derivative. This is presumably the effect of symmetry.

With the variation of He and Ar pressure there appears some weak bands both in the longer as well as the shorter wavelength side of the origin transition. Those bands are represented by * in the FE spectra. The decay profiles of these bands in time resolved study are seen to be biexponential, one lifetime component being shorter than that of the bare molecule, while other bands of the FE spectra ascribed to the bare molecule, have a single exponential decay. The dynamics and spectra of such Ar and He clusters will be reported elsewhere.

IV. CONCLUSION

The FE spectrum of HHP bears the signature of the two conformers of nearly equal population. Out of the two 0–0 bands, the longer wavelength one is associated with the chair (*trans*) form and the other with the boat (*cis*) form. This conclusion is arrived at by combining SVL spectra with symmetry-based selection rules and calculated S_0 frequencies of vibrational modes. Accurate *ab initio* calculations are needed to explain the energy difference between chair, planar and boat forms. The low-frequency vibronic bands have been tentatively assigned. The lifetimes of low-frequency vibronic levels follow the trend reported by Jacobson *et al.* for naphthalene monoderivatives,^{8(b)} namely, they fluctuate at low excess energies, but merge and decrease steadily at high energies of excitation.

Note added in proof. Hole-burning spectra recently obtained by us indicate that our calculated barrier between the two forms is much too high. This will be discussed elsewhere.

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