Two-Photon Fluorescence Excitation Spectrum of 1,6-Methano-[10]annulene

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The two-photon fluorescence excitation spectrum of 1,6-methano-[10]annulene has been measured in fluid solution at room temperature between 25 000 and 40 000 cm^{-1} and in rigid solution at 77 and 15 K between 25 000 and 28 000 cm^{-1}. The two-photon polarization ratios of both spectra have been determined. Spectral assignments have been made on the basis of two-photon polarization data, ab initio calculations, and comparison with one-photon data. The four excited states below 5 eV have been identified. Calculated one- and two-photon allowed intensities are in good agreement with results derived from the alternant hydrocarbon theory. The $S_0 \rightarrow S_1$ two-photon intensity is mainly vibronically induced by b_1 modes. The most active b_1 vibration, the "Kekule"-type mode responsible for double bond localization in 1,6-methano-[10]annulene, shifts to ≈1540 cm^{-1} in S_1 from the ground state 1355 cm^{-1} value. Applying two-photon polarization results to 1,6-methano-[10]annulene (C_{2v} symmetry), the tensor elements of the strongest totally symmetric $S_0 \rightarrow S_1$ ($B_1 \times b_1 \times a_1$) transition have been estimated.

I. Introduction

Two-photon absorption processes in aromatic molecules have stimulated a large amount of experimental and theoretical work.[1−4] Being simple aromatics (benzene, naphthalene, pyrene, ...), centrosymmetric, vibronic levels of total gerade symmetry have been probed in the lowest excited state.[5−14] A major result of these studies was the observation of a strong false origin dominating the $S_0 \rightarrow S_1$ two-photon spectrum. The vibronic coupling between the ground and the final state through ungerade vibrations was first inferred[6] and then found to be responsible of the effect in a number of papers.[15−17] This feature was recognized as a part of a general behavior relating the spectroscopy of aromatic systems to their alternant hydrocarbon nature.[18] On the basis of pseudoparity symmetry and perturbation selection rules,[19,20] one- and two-photon transitions were shown to be differently enhanced with respect to inductive and vibronic effects.[18,21]

Extension of two-photon experiments to higher homologues of benzene, i.e., $[4n + 2]$-annulenes with $n \geq 2$, has not been attempted so far. The ground state properties and reactivity of many of these systems have been characterized both experimentally and theoretically.[22,23] However, detailed information on the excited $\pi\pi^*$ states is actually scarce and the spectral analysis in terms of pseudoparity symmetry difficult. Recently, well-resolved one-photon fluorescence $S_1 \rightarrow S_0$ and fluorescence excitation $S_0 \rightarrow S_1$ spectra of 1,6-methano-[10]-annulene in condensed phase have been reported.[24] On the whole, one-photon spectroscopy conforms to the aromatic behavior.[25−29] Related one-photon studies have been performed on [14]-annulene[30] and ethano-bridged [14]annulene.[31] Equivalent two-photon studies are recommended to test the alternant hydrocarbon model in higher annulenes.

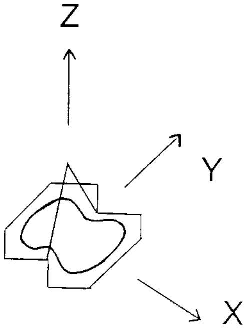

Figure 1. Molecular structure of 1,6-methano-[10]annulene and the reference axis system.

Here a two-photon absorption study of 1,6-methano-[10]-annulene (see Figure 1) in solution at room temperature in the range 25 000−40 000 cm^{-1} and at low temperature in the region of the first electronic transition is reported. Two−photon polarization ratios of fluid and rigid solutions have been determined following known procedures.[1,32−38] The experimental data are compared with theoretical two-photon results derived from ab initio calculations.

II. Experimental Section

1,6-Methano-[10]-annulene was a generous gift from Prof. E. Vogel (University of Köln, Germany). Details on the sample conservation and on the preparation of fluid and rigid solutions in isopentane/diethyl ether (7:3) mixtures as well as on the experimental apparatus have been already reported.[24] Additional points relevant to present experiments are the following. Two-photon measurements were carried out on 10^{-2} M solutions with laser radiation, tunable in the wavelength range 800−520 nm, from an OPO system pumped by the third harmonic of a Nd:YAG laser operating at 10 Hz. Linearly and circularly polarized light of equal intensity was obtained by the combination of three Fresnel rhombs, according to a known optical setup.[39] The two-photon-induced fluorescence signal was filtered through a blue transmitting optical glass and a $CuSO_4$ aqueous solution and then checked to be quadratic as a function of the incident intensity. Polarized two-photon experiments on rigid glassy solutions at 77 K have been performed using linearly (vertical,

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V, or ↑↑) polarized incident light and observing the linearly polarized fluorescence signal, collected at 90° with respect to the excitation beam [analyzer in front of the photomultiplier oriented to pass vertically (V) or horizontally (H) polarized light].[38] The polarization bias of the fluorescence anisotropy was taken into account by measuring the signal with excitation and fluorescence light horizontally polarized and with excitation horizontally and fluorescence vertically polarized. The ratio of the two intensities must be unity.[36] The correction factor was ≤10% in our experiments. Experiments at 15 K were performed condensing a small drop of the solution on the cold tip of a closed-circuit He cryostat. The two-photon excitation spectra are normalized to a reference signal taken by diverting a small portion of the incident light on a photodiode.

III. Results

A. Two-Photon Processes: Intensity and Polarization Ratio. In the dipole approximation the strength of the two-photon transition from the ground $|g\rangle$ to the excited $|f\rangle$ state, due to incident photons of equal energy ω_0, is determined by the tensor **S** whose elements in a molecular reference frame are[1−4]

$$S_{\alpha\beta} = \sum_i \frac{(\alpha_{gi}\beta_{if} + \beta_{gi}\alpha_{if})}{\omega_{gi} - \omega_0} \qquad \alpha, \beta = x, y, z \tag{1}$$

being $\alpha_{gi} = \langle g|\mu_\alpha|i\rangle$, $\beta_{if} = \langle i|\mu_\beta|f\rangle$ and correspondingly for the other two factors and ω_{gi} the energy of the intermediate states $|i\rangle$ with respect to $|g\rangle$. Assuming for 1,6-methano-[10]annulene a C_{2v} symmetry, as will be better justified in the next section, the two-photon tensor is decomposed into A_1, A_2, B_1, B_2 irreducible representations

$$\mathbf{S}(A_1) \equiv \begin{pmatrix} S_{xx} & & \\ & S_{yy} & \\ & & S_{zz} \end{pmatrix} \qquad \mathbf{S}(A_2) \equiv \begin{pmatrix} & S_{xy} & \\ S_{yx} & & \\ & & \end{pmatrix}$$

$$\mathbf{S}(B_1) \equiv \begin{pmatrix} & & S_{xz} \\ & & \\ S_{zx} & & \end{pmatrix} \qquad \mathbf{S}(B_2) \equiv \begin{pmatrix} & & \\ & & S_{yz} \\ & S_{zy} & \end{pmatrix}$$

with $S_{yx} = S_{xy}$, $S_{xz} = S_{zx}$, $S_{yz} = S_{zy}$. Electronic (or vibronic) states of any, i.e., A_1, A_2, B_1, B_2, symmetry species may be reached from $|g\rangle$.

It has been further recognized since early two-photon fluorescence studies that for randomly oriented molecules the two-photon intensity depends on the polarization of the incident photons[1,32−34] and in the case of random, nonrotating species, i.e., rigid solutions, also on that of the fluorescent photon.[35] The case of a two-photon process followed by one-photon fluorescence has been considered in several papers[36−38] since the original treatment of McClain.[35] It has been found that the emission intensity depends on molecular quantities such as the two-photon absorption tensor **S** and the fluorescence transition dipole F, on the incident i and viewing v polarization vectors, and on the average process over all molecular orientations, according to the following expression[36]

$$I_i^v = a_i^v\,\delta_G + b_i^v\,\delta_F + c_i^v|F\cdot\mathbf{S}|^2 + d_i^v(F\cdot\mathbf{S}\cdot F)\mathrm{Tr}(\mathbf{S}) \tag{2}$$

where a_i^v, b_i^v, c_i^v, d_i^v, are polarization factors related to the experimental geometry, whose values are collected in Table 1, while $\delta_G = \sum_{\alpha\beta} S_{\alpha\beta}S_{\alpha\beta}$, $\delta_F = \sum_{\alpha\beta} S_{\alpha\alpha}S_{\beta\beta}$, and $\mathrm{Tr}(\mathbf{S}) = \sum_{\alpha\alpha} S_{\alpha\alpha}$. Four independent experiments may be envisaged using linearly (↑↑, V) and circularly (⊃⊃, C) polarized incident light and selecting linearly polarized (↑, V, or →, H) fluorescence, 90° to the direction k of the incoming beam. These may be denoted, with slightly different symbols than previously used,[36,38] as I_V^V, I_V^H, I_C^V, I_C^H, respectively, where the subscripts label incident and superscripts fluorescence polarization. In this work, the I_V^V and I_V^H two-photon intensities of rigid solutions have been measured.

TABLE 1: Two-Photon Intensities of Rigid and Fluid Solutions (Upper and Lower Entries, Respectively)[a]

	a_i^v	b_i^v	c_i^v	d_i^v
I_V^V	2	1	8	4
I_V^H	6	3	−4	−2
I_C^V	5	−1	6	−4
I_C^H	11	−5	−12	8
	a_i	b_i		
I_V	2	1		
I_C	3	−1		

[a] The polarization parameters have been calculated from eq 2 in the first case and from equation $I_i = a_i\delta_G + b_i\delta_F$ of ref 1 in the second.

TABLE 2: Polarization Ratios for Two-Photon Studies of C_{2v} Molecules[a]

	rigid solutions I_V^H/I_V^V	fluid solutions Ω
A_1	$(3a^2 + 4a + 9)/(15a^2 + 6a + 3)$	$(2a^2 - 2a + 2)/(3a^2 + 2a + 3)$
A_2	2/3	3/2
B_1	2/3	3/2
B_2	3	3/2

[a] The results are expressed in terms of $a = S_{xx}/S_{yy}$ and assuming $S_{zz} = 0$.

Several polarization ratios may be defined for each symmetry species of the two-photon tensor **S**. With reference to I_V^H/I_V^V, since this quantity depends on the transition dipole F, which is long-axis, i.e., x, polarized for 1,6-methano-[10]annulene,[24,27] only the case corresponding to $F \equiv (1\ 0\ 0)$ will be considered. The results are reported in Table 2, where it has been assumed $S_{zz} = 0$, as suggested from the fact that this tensor element is negligible with respect to S_{xx} and S_{yy} for aromatic systems in condensed phase.[15−17,36] The polarization ratio of totally symmetric transitions depends on the relative strength of S_{xx} and S_{yy}, i.e., on the factor $a = S_{xx}/S_{yy}$, as can be seen from Figure 2. In contrast, non-totally symmetric transitions have fixed ratios. Among these latter, A_2 and B_1 may be easily discriminated from B_2 by means of I_V^H/I_V^V.

Finally, when the emission is isotropic, for instance for fluid solutions, the two-photon intensity is no longer depending on the viewing polarization direction and the two intensities, I_V and I_C, are related only to δ_F and δ_G, according to the coefficients of Table 1.[1] In this case the ratio $\Omega = I_C/I_V$ differentiates between totally and non-totally symmetric transitions, being for the former smaller than $^3/_2$ as a function of a (see Table 2 and Figure 2) and $^3/_2$ for the latter.

B. Two-Photon Excitation Spectra. The two-photon excitation spectrum of 1,6-methano-[10]annulene between 25 000 and 40 000 cm^{-1} at room temperature and exciting with linearly polarized light is shown in Figure 3. The polarization ratio Ω is displayed on the top of the figure. For the sake of comparison, the one-photon spectrum is also reported in the same figure. The two-photon spectrum has a weak and structured intensity in the region 25 000−30 000 cm^{-1} and a strong band around 39 300 cm^{-1}, in good correspondence with the first and the third

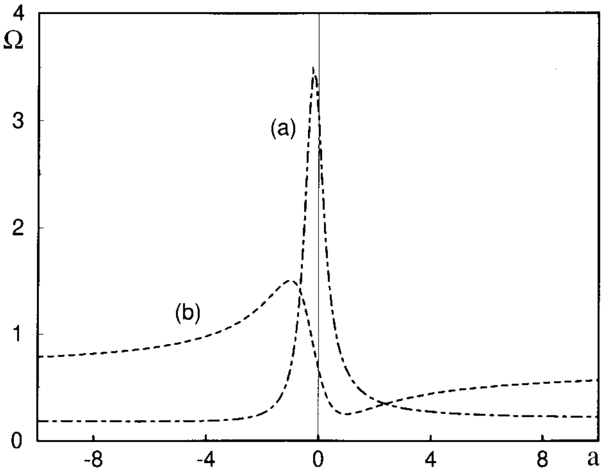

Figure 2. Polarization ratios of two-photon $A_1 \rightarrow A_1$ transitions for C_{2v} molecules as a function of $a = S_{xx}/S_{yy}$ and assuming $S_{zz} = 0$. Rigid solutions: (a) I^{H}_{V}/I^{V}_{V}; fluid solutions: (b) I_C/I_V.

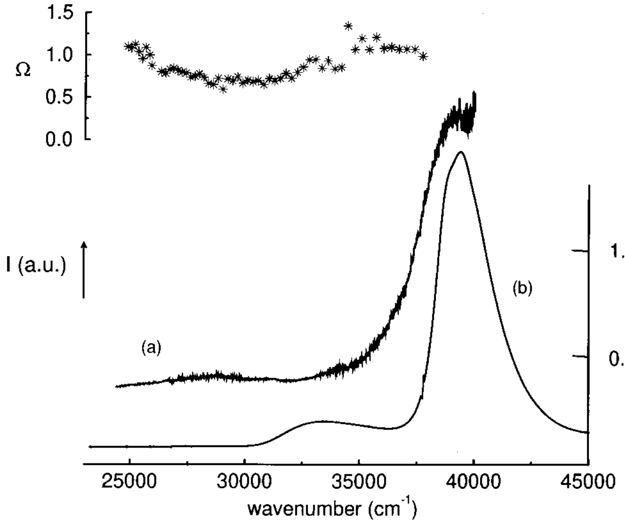

Figure 3. Two-photon excitation spectrum [(a), left, linear polarization] and polarization ratio Ω of 1,6-methano-[10]annulene 10^{-2} M in isopentane/diethyl ether (7:3) solution at room temperature in the energy range 25 000−40 000 $\mathrm{cm^{-1}}$. For the sake of comparison also the one-photon solution spectrum [(b), right], 10^{-5} M in cyclohexane, is shown in the same experimental conditions.

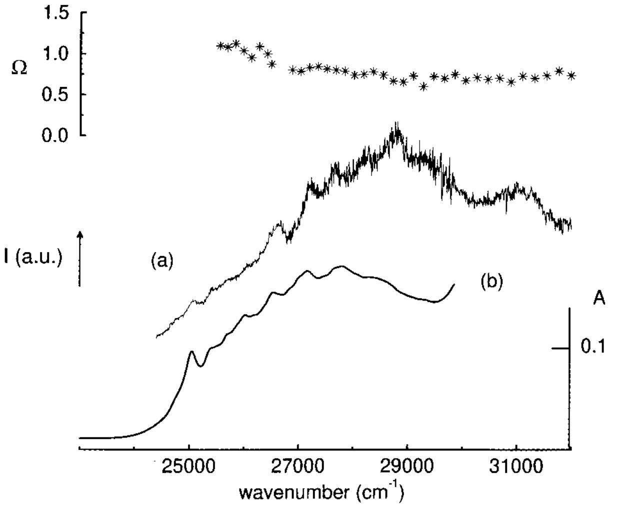

Figure 4. Enlarged view of the two-photon excitation spectrum [(a), left, linear polarization] and polarization ratio Ω of 1,6-methano-[10]-annulene 10^{-2} M in isopentane/diethyl ether (7:3) solution at room temperature in the energy range 25 000−30 000 $\mathrm{cm^{-1}}$. For the sake of comparison also the one-photon solution spectrum [(b), right], 10^{-2} M in isopentane/diethyl ether (7:3), is shown in the same experimental conditions.

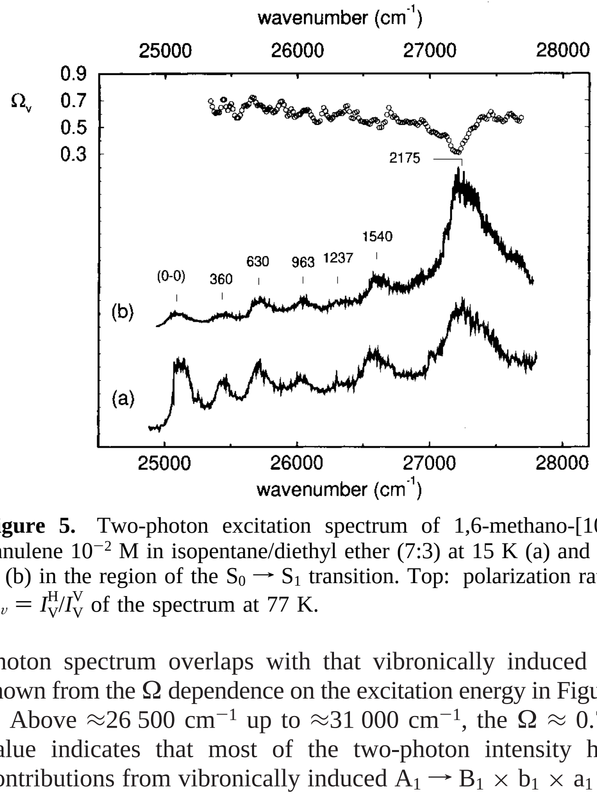

Figure 5. Two-photon excitation spectrum of 1,6-methano-[10]-annulene 10^{-2} M in isopentane/diethyl ether (7:3) at 15 K (a) and 77 K (b) in the region of the $S_0 \rightarrow S_1$ transition. Top: polarization ratio $\Omega_v = I^{H}_{V}/I^{V}_{V}$ of the spectrum at 77 K.

one-photon absorption bands, respectively. On the contrary, no clear two-photon counterpart to the one-photon band centered around 33 500 $\mathrm{cm^{-1}}$ is observed. The slow increase of Ω above 32 500 $\mathrm{cm^{-1}}$ may, however, suggest that a weak non-totally symmetric transition is occurring in this energy range. There are strong theoretical indications, corroborated also by our own calculations of this work, in favor of an assignment of the one-photon spectrum to the lowest three $\pi\pi^*$ states, $S_1(B_1)$, $S_2(B_2)$, $S_3(B_1)$. In other words, no hidden, i.e., inactive (A_2) or very weakly active, states are predicted up to 39 000 $\mathrm{cm^{-1}}$. The lowest two-photon region has been therefore assigned only to the $S_0 \rightarrow S_1(B_1)$ transition. The one- and two-photon spectra in this range (25 000−30 000 $\mathrm{cm^{-1}}$) are shown in Figure 4. S_1 being of B_1 symmetry, the origin band is expected to be active in both and, in fact, is observed at 25 050 and 25 070 $\mathrm{cm^{-1}}$, respectively. The two spectra exhibit appreciable, though not well resolved, vibronic structure. The one-photon data have been already analyzed in detail.[24] The one-photon $S_0 \rightarrow S_1$ spectrum is Franck−Condon allowed with activity of the totally symmetric vibrations related to the change of molecular geometry upon excitation. On the contrary, the allowed portion of the two-photon spectrum overlaps with that vibronically induced as shown from the Ω dependence on the excitation energy in Figure 4. Above ≈26 500 $\mathrm{cm^{-1}}$ up to ≈31 000 $\mathrm{cm^{-1}}$, the $\Omega \approx 0.75$ value indicates that most of the two-photon intensity has contributions from vibronically induced $A_1 \rightarrow B_1 \times b_1 \times a_1 = A_1$ transitions. As Ω smoothly increases below ≈26 500 $\mathrm{cm^{-1}}$, this may be taken as plausible evidence that allowed $A_1 \rightarrow B_1 \times a_1$ transitions are observed.

On decreasing the temperature, the vibronic structure of the first absorption region becomes sharper than at room temperature. The two-photon spectrum between 25 000 and 28 000 $\mathrm{cm^{-1}}$ is shown in Figure 5. Beyond the electronic origin, around 25 085 $\mathrm{cm^{-1}}$ at 77 K a weak allowed $B_1 \times a_1$ structure, with peaks at 360, 630, 963, and 1237 $\mathrm{cm^{-1}}$ from the origin, is observed, as indicated by the polarization ratio I^{H}_{V}/I^{V}_{V} close to $^2/_3$. This confirms that the lowest portion of the $S_0 \rightarrow S_1$ absorption is due to totally symmetric additions to (0−0). Two stronger bands occur at higher energy (1540 and 2175 $\mathrm{cm^{-1}}$,

TABLE 3: Observed (One-Photon) and Calculated Vertical Transition Energies (ΔE, eV) and Oscillator Strengths ($f_{S_0 \to S_n}$) of the Lowest $\pi\pi^*$ Excited States of 1,6-Methano-[10]Annulene[a]

	ΔE		$f_{S_0 \to S_n}$		
	obsd[b]	calc	obsd[b]	calc	configurations
$S_1(B_1)$	3.44	3.33	0.003	5×10^{-6}	(H − 1; L) − (H; L + 1)
$S_2(B_2)$	4.16	4.39	0.107	0.003	(H; L)
$S_3(B_1)$	4.87	4.65	1.04	1.64	(H − 1; L) + (H; L + 1)
$S_4(A_1)$		4.89		8×10^{-6}	(H − 2; L + 1) − (H − 1; L + 2)
$S_5(A_2)$		5.68			(H; L + 2) − (H − 2; L)
$S_6(A_2)$		5.80			(H; L + 2) + (H − 2; L) (H − 3; L + 1) + (H − 1; L + 3)
$S_7(A_1)$		6.38		1.5×10^{-5}	(H; L + 3) − (H − 3; L) (H − 2; L + 1) − (H − 1; L + 2)
$S_8(B_1)$		6.89		0.25	(H − 4; L) − (H; L + 4)
$S_9(B_2)$		6.97		0.07	(H − 1; L + 4) − (H − 4; L + 1)

[a] The calculated MCSCF/CAS values (6-31G basis set; 10 e$^-$, 10 π MO) have been corrected by the MC/QDPT perturbation treatment. In the last column the main excited (+) and (−) configurations contributing to the $\pi\pi^*$ states are reported (H = HOMO; L = LUMO). [b] From ref 25.

77 K), the second corresponding to a pronounced minimum of I_V^H/I_V^V at 77 K, ≈0.3. This clearly supports the $A_1 \rightarrow A_1$ assignment for the 2175 cm^{-1} band on the basis of Table 2. Comparison of the polarization data on this band in fluid and rigid solution with data of Figure 2 gives for $a = S_{xx}/S_{yy}$ a value in the range −2 (rigid)/−8 (fluid). Possible depolarizing effects, such as the not complete randomization of the excited molecules prior to emission,[18] and/or background two-photon intensity due to non-totally symmetric transitions, may be the origin of the discrepancy between the two a values. Despite of this, it should be appreciated the common indication of both experiments about S_{xx} and S_{yy} of opposite sign with $|S_{xx}| > |S_{yy}|$. This band being of A_1 symmetry, the only possible assignment is as a vibronic $B_1 \times b_1 \times a_1$ transition built on a false origin at lower energy, i.e., on the 1540 cm^{-1} band.

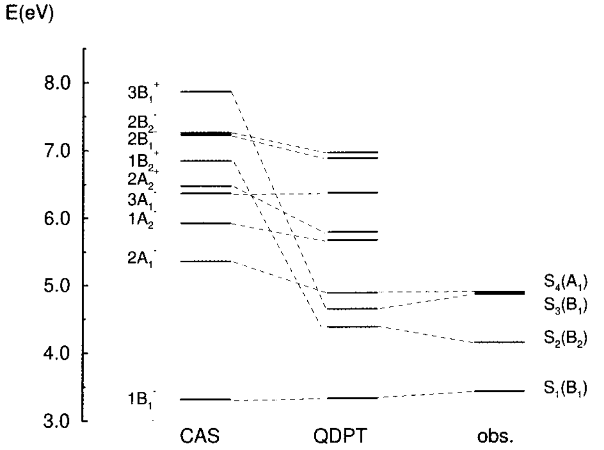

Figure 6. Calculated and observed vertical transition energies (eV) of 1,6-methano-[10]annulene. Left: MCSCF/CAS values (6-31G basis set; 10 e$^-$, 10 π MO) of the lowest electronic states denoted by the symmetry and pseudoparity (+, −) labels of Table 3; center: values corrected with the MC/QDPT perturbation treatment of ref 44; right: observed one- and two-photon transitions, from ref 25 and this work.

IV. Discussion

A. One-Photon Excitation Energies and Intensities. It has been already shown at the RHF level of theory that three ground state extrema occur for 1,6-methano-[10]annulene, with aromatic (C_{2v}), polyenic (C_s), and norcaradienic (C_{2v}) geometries.[24,40] The former is the only minimum including electronic correlation, in excellent agreement with experiment.[41] Excited state calculations were performed at the MCSCF/CAS ground state geometry of the aromatic isomer, promoting 10 electrons among the 10 MO's with the largest p_z contribution from the ring C atoms. The CAS-CI vertical excitation energies were corrected with the multireference perturbation treatment (MC/QDPT) included in the GAMESS program,[42,43] intended to account for dynamic electronic correlation.[44] Calculated excitation energies and oscillator strengths are collected in Table 3 together with the main configurations of each excited state. Excitation energies match satisfactorily with experiment,[25] thus giving confidence for their use in the discussion of two-photon results of the next subsection. Oscillator strengths, weaker than observed for S_1 and S_2, are nevertheless in qualitative agreement with experimental results. As to the nature of the lowest excited $\pi\pi^*$ states of 1,6-methano-[10]annulene, it is interesting to note that they have large contributions from "plus" and "minus" combinations of singly-excited configurations. An approximate "plus" (+) and "minus" (−) symmetry ("pseudoparity") may be assigned to such states, following Pariser proposal for alternant hydrocarbons.[19] In summary, in the simple Huckel approximation $\pi\pi^*$ states are represented by (+) and (−) combinations of singly-excited degenerate (i, j') and (j, i') configurations, i, i' as well as j, j' being molecular orbitals with energies symmetrically located with respect to the Coulomb integral α. Further, the ground state behaves as a (−) state while nondegenerate (i, i') and (j, j') configurations as (+) states. In this model, $\pi\pi^*$ states may be grouped into two main classes, (+) and (−), according to their pseudoparity behavior. Only states of different pseudoparity may be one-photon active, i.e., (+) ↔ (−). Although pseudoparity symmetry is lost on going from the Huckel to CAS representation of $\pi\pi^*$ states, the large participation of singly-excited configurations to the CAS wave function suggests that the previous results may be approximately valid also in the latter case. For instance, it has been found that, among the lowest nine excited states of 1,6-methano-[10]annulene, only $S_2(B_2)$ and $S_3(B_1)$, having pronounced (+) symmetry and $S_6(A_2)$, (+) to a lesser extent, move downward their excitation energy switching on the perturbation. On the contrary, the corresponding shift of all other states, which are mostly (−), is much smaller, as may be seen from Figure 6. This is quite in agreement with the observation that "minus" or covalent states are not appreciably dependent on the electronic correlation, while "plus" or ionic states undergo a large shift from their CAS-CI energy values when the perturbation correction is considered.[44] The combined effect gives a qualitatively correct correlation with the observed excited-state energies (see Figure 6). Second, the strongest one-photon transitions from the ground (−) state are expected to be $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ due to their (+) symmetry, again in agreement with experimental evidence (see Figure 3).

TABLE 4: Observed (Two-Photon) and Calculated Vertical Transition Energies (Δ*E*, eV) and Two-Photon Intensities ($I_{V,S_0\to S_n}$) of the Lowest ππ* Excited States of 1,6-Methano-[10]annulene[a]

	Δ*E*		$I_{V,S_0\to S_n}$		
	obsd	calc	obsd	calc	configurations
$S_1(B_1)$	3.47	3.33	0.08	0.337	(H − 1; L) − (H; L + 1)
$S_2(B_2)$	4.09[b]	4.39	n.a.[c]	10^{-3}	(H; L)
$S_3(B_1)$		4.65	n.a.[c]	0.024	(H − 1; L) + (H; L + 1)
$S_4(A_1)$	4.87	4.89	1	1	(H − 2; L + 1) − (H − 1; L + 2)
$S_5(A_2)$		5.68		10^{-7}	(H; L + 2) − (H − 2; L)
$S_6(A_2)$		5.80		0.908	(H; L + 2) + (H − 2; L) (H − 3; L + 1) + (H − 1; L + 3)
$S_7(A_1)$		6.38		3.83	(H; L + 3) − (H − 3; L) (H − 2; L + 1) − (H − 1; L + 2)
$S_8(B_1)$		6.89		0.194	(H − 4; L) − (H; L + 4)
$S_9(B_2)$		6.97		0.013	(H − 1; L + 4) − (H − 4; L + 1)

[a] The two-photon intensities $I_{V,S_0\to S_n}$ are relative to $I_{V,S_0\to S_4}$. The calculated MCSCF/CAS values (6-31G basis set; 10 e⁻, 10 π MO) have been corrected by the MC/QDPT perturbation treatment. In the last column the main excited (+) and (−) configurations contributing to the ππ* states are reported (H = HOMO; L = LUMO). [b] From the Ω dependence on wavenumber. [c] n.a. = not appreciable.

B. Two-Photon Excitation Energies and Intensities. The two-photon spectrum of 1,6-methano-[10]annulene may be understood on the basis of the approximate pseudoparity symmetry exhibited by the lowest ππ* excited states. Allowed two-photon transitions occur between states of equal pseudoparity, i.e., (+) → (+) and (−) → (−).[18] For excitation energies below 5 eV, the only ππ* states with (−) symmetry are S_1 and S_4 and accordingly the most active two-photon transitions from the (−) ground state are expected to be $S_0 \to S_1$ and $S_0 \to S_4$. In view of this argument it is questionable to assign the strongest two-photon band centered at 39 300 cm^{-1} to $S_0 \to S_3$ despite the close proximity of the one- and two-photon absorption maxima (see Figure 3). Since from our calculations it results that the vertical $S_0 \to S_3$ and $S_0 \to S_4$ energies are almost degenerate, a more straightforward choice for assignment would be the latter, i.e., $S_0 \to S_4(A_1)$. It may be noted that a mutual exclusion rule holds approximately for the lowest ππ* states of noncentrosymmetric 1,6-methano-[10]annulene, S_2 and S_3 being more active in one-photon and S_1 and S_4 in two-photon spectroscopy. The conclusion is supported by the calculation of two-photon intensities based on our CAS/CI results. The two-photon intensity of the $|g\rangle \to |f\rangle$ transition using linearly polarized light is given by the expression[1] $I_V \propto 2\delta_F + 4\delta_G$, δ_F and δ_G having been previously defined. All the transition moments $S_n \to S_m$ between the lowest nine excited states have been calculated in order to obtain the two-photon tensor elements $S_{\alpha\beta}$ from eq 1. It is confirmed that for the two $A_1 \to A_1$ transitions here considered S_{zz} is vanishingly small with respect to S_{xx} and S_{yy}, in agreement with the assumption of section III. The results are collected in Table 4. Because of the limited number of intermediate states entering the calculation, the values of Table 4 depend on this number[45] and should accordingly be taken only as a semiquantitative indication of the two-photon activity. The relative two-photon intensities of the four lowest transitions are, however, in agreement with predictions based on pseudoparity and, more important, with experimental results. Despite the calculation limits, it is felt that they account fairly for the observed intensities.

TABLE 5: b_{2u} Modes of Benzene (B), b_{3u} Modes of Naphthalene (N, Long-Axis Polarized), and b_1 Modes of 1,6-Methano-[10]annulene (MA; Long-Axis Polarized, See Figure 1) in S_0 and S_1[a,b,c]

b_{2u}		b_{3u}		b_1	
B		N		MA	
S_0	S_1	S_0	S_1	S_0	S_1
1241	1291	687	662	359*i*[d]	390
1359	**1860**	1068	989	452	443
		1223	1249	676	692
		1309	1349	735	715
		1462	1599	842	890
		1657	**1819**	989	952
				1116	1123
				1263	1311
				1385	1374
				1434	1592
				1665	**1975**

[a] Unscaled calculated frequencies (cm^{-1}) have been obtained after geometry optimization by means of the MCSCF/CAS procedure (B: 6 e⁻, 6 π MO; N, MA: 10 e⁻, 10 π MO; 6-31G basis set). [b] Boldface frequencies identify "Kekule"-type vibrations. $E(S_0,B) = -230.700\,756$ au, $E(S_1,B) = -230.525\,681$ au; $E(S_0,N) = -383.351\,540$ au, $E(S_1,B) = -383.202\,933$ au; $E(S_0,MA) = -422.271\,300$ au, $E(S_1,MA) = -422.164\,878$ au. [c] The geometries of these states as well as the frequencies of all remaining vibrational modes are available on request. [d] At the MCSCF/CAS level of theory here considered (10 e⁻, 10 π MO) the ground state minimum has polyenic (C_s) structure (see ref 24). The aromatic C_{2v} structure is the only minimum when the density functional approach is used (see ref 41).

Following pseudoparity considerations, it should be expected also that the two-photon vibronic activity of 1,6-methano-[10]-annulene in S_1 is efficient. In fact, vibronic perturbations, i.e., related to the Hamiltonian dependence on the normal coordinates, couple states of equal pseudoparity[18] and as a consequence strengthen the $S_0 \to S_1(B_1^-)$ transition with intensity borrowing from other (−) → (−) two-photon transitions. The wide absorption region of the solution spectrum with $\Omega \approx 0.75$ may thus be justified. With reference to centrosymmetric aromatic molecules, it is, on the other hand, a general experimental result that their lowest excited (−) state (L_b^- in Platt nomenclature) is associated with vibronic spectra mostly due to false origins of A_g symmetry.[5−14] These have been assigned to "Kekule"-type C−C vibrations with frequencies higher in S_1 than in S_0.[6,15−17] The b_1 frequencies of our molecule, the b_{2u} frequencies of benzene, and the b_{3u} frequencies of naphthalene in S_0 and S_1 have been determined after geometry optimization by means of the MCSCF/CAS procedure (6-31G basis set; 6 e⁻, 6 π MO for benzene (B), 10 e⁻, 10 π MO for naphthalene (N) and 1,6-methano-[10]annulene) and reported in Table 5. Our calculation on benzene and naphthalene is in substantial agreement with that of a past report.[46] The vibrational analysis shows that the b_{2u} vibration 1359 (B) cm^{-1} and the b_{3u} vibration 1462 (N) cm^{-1} shift to 1860 (B) and 1599 (N) cm^{-1} in the excited state. Their displacements favor double bond localization for both molecules, as seen in Figure 7, thus matching significantly the transition density matrices between ground and L_b^- states, $\rho_{S_0;L_b^-}$, calculated following known theoretical methods.[18,21,47] In the case of 1,6-methano-[10]annulene the same procedure gives the correlation between the 1434 cm^{-1} (S_0) and the 1975 cm^{-1} (S_1) b_1 modes. Using similar considerations it may be seen from the same Figure that there is a sufficiently good overlap between $\rho_{S_0;B_1^-}$ and the 1434 cm^{-1} b_1 normal coordinate, suggesting that this mode is responsible of the two-photon vibronic activity in S_1. Experimentally, the "Kekule"-type mode is observed in the infrared[41] at 1355 cm^{-1} and associated with the 1540 cm^{-1} peak of our two-photon spectrum. The theoretical overestimate of the frequency shift in benzene and naphthalene has been attributed to the absence of polarization functions in the atomic basis set.[46] Most likely, it is necessary to include these functions also in the case of 1,6-methano-[10]annulene.

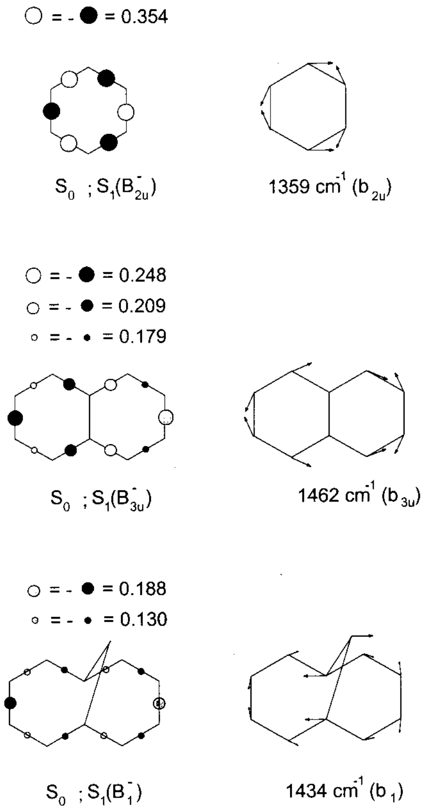

Figure 7. Left: transition density matrices between the ground (S_0) and the lowest excited state of benzene, naphthalene and 1,6-methano-[10]annulene [$S_1(B_{2u}^-)$, $S_1(B_{3u}^-)$, and $S_1(B_1^-)$, respectively]. Only one-center and nearest-neighbor two-center terms are shown. Right: C−C stretching modes 1359 cm^{-1} (B, b_{2u}), 1462 cm^{-1} (NA, b_{3u}) and 1434 cm^{-1} (MA, b_1). The transition density calculations have been made following refs 18, 21, and 47, on the basis of our MCSCF/CAS results on the three molecules.

Additional information about the S_0/S_1 coupling in 1,6-methano-[10]annulene through the 1434 cm^{-1} mode may be obtained from the experimental energy shift of ≈ 185 cm^{-1}. It is customary to describe the frequency increase from S_0 to S_1 in these systems by a two-state model.[11,16,17,48] This assumes that the two states in our case interact through b_1 modes with the coupling coefficient $\langle S_1|\partial H/\partial q_{b_1}|S_0\rangle = V_{10}$, giving origin to ground (ν_-) and excited (ν_+) state frequencies. The fractional change $\Delta\nu/\nu$ with respect to the unperturbed value ν, taken as the average of ν_+ and ν_-, results to be[16]

$$\frac{\Delta\nu}{\nu} \approx 2\frac{{V_{10}}^2}{\Delta E_{10}k}$$

where ΔE_{10} is the transition energy between S_0 and S_1 and k the unperturbed force constant. From this expression, the coupling coefficients V_{10} for the most active b_{2u} (b_{3u}) C−C stretching vibrations of benzene (naphthalene) in the two-photon spectrum may be derived. In the case of benzene this is observed at 1570 cm^{-1} in S_1[49,50] and correlated with that at 1310 cm^{-1} [6,50,51] in S_0, so that we have $\nu = 1440$ cm^{-1} and $\Delta\nu/\nu = 0.18\,055$. Since in addition k is estimated from our calculations ≈7 mdyn/Å and $\Delta E_{10} \approx 4.77$ eV, it results that $V_{10} \approx 4.35$ eV/Å. Repeating the calculation for naphthalene ($\nu_+ = 1555$ cm^{-1} and $\nu_- = 1398$ cm^{-1} following past assignments;[9,16] $k \approx 4.3$ mdyn/Å, $\Delta E_{10} \approx 3.97$ eV) it is found $\Delta\nu/\nu = 0.10\,633$ and $V_{10} \approx 2.4$ eV/Å, in good agreement with the reported value.[16] Finally, in the case of 1,6-methano-[10]annulene since $\nu_+ = 1540$ cm^{-1} and $\nu_- = 1355$ cm^{-1} and $\Delta E_{10} \approx 3.1$ eV and $k \approx 3.8$ mdyn/Å, the experimental energy difference of 185 cm^{-1} is reproduced with $V_{10} \approx 2.15$ eV/Å, i.e., a value close to that of naphthalene, as reasonably expected.

V. Conclusions

In this paper, we have reported on the two-photon properties of 1,6-methano-[10]annulene, the bridged higher homologue of benzene with 10 π electrons. The two-photon fluorescence excitation spectrum at room temperature in fluid and at low temperature in rigid solution has been determined together with the polarization ratio. Two major results of this study are as follows:

1. The one- and two-photon spectroscopies of 1,6-methano-[10]annulene are well described within the pseudoparity symmetry of the alternant hydrocarbon model.[18]
2. Accurate vertical transition energies of the four lowest $\pi\pi^*$ transitions have been obtained with the use of MCSCF/CAS wave functions coupled with multireference perturbational methods.[44]

The combination of points 1 and 2 together with one- and two-photon intensity calculations allows to make a definite assignment of the lowest excited states below 5 eV.

As in centrosymmetric aromatics, the $S_0 \rightarrow S_1(B_1)$ two-photon intensity is mostly induced by the “Kekule”-type b_1 vibration, i.e., the mode responsible of double bond localization in 1,6-methano-[10]annulene. This follows from comparison of the vibrational frequencies of our molecule with those of benzene and naphthalene in S_0 and S_1.

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