Electronic Spectra of Porphycenes in Rare Gas and Nitrogen Matrices

Alexander Starukhin,[†,‡] Emanuel Vogel,[§] and Jacek Waluk*,[†]

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland, Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus, F. Scaryna Avenue 70, 220072 Minsk, Belarus, and Institut für Organische Chemie der Universität, Greinstrasse 4, D-50939 Köln, Germany

Fine-line electronic absorption and fluorescence spectra of porphycene and 2,7,12,17-tetra-*n*-propylporphycene have been measured in low-temperature nitrogen, argon, krypton, and xenon matrices. A well-resolved emission spectrum of porphycene was also obtained in an isotropic glassy matrix using the fluorescence line-narrowing technique. Analysis of the observed matrix spectral shifts enabled the assignment of the origin of the S_0-S_2 electronic transition. Vibrational frequencies have been obtained for the ground and two lowest excited singlet states. Vibronic and site structure in the region of S_0-S_1 and S_0-S_2 electronic transitions of porphycenes have been compared with the corresponding data for porphyrin. Both similarities and differences were observed. In particular, contrary to the case of porphyrin and its derivatives, no site structure was observed in the spectra of porphycenes in xenon and krypton matrices. This was explained by a model that takes into account different positions of the transition moment directions in the two chromophores with respect to the matrix cage. No evidence was obtained for the presence of the *cis* tautomeric forms of porphycene.

Introduction

Porphyrins and metalloporphyrins continue to be a subject of intense interdisciplinary research. Due to the crucial role these molecules play in biological processes such as photosynthesis, oxygen transport, and activation, they have been labeled "pigments of life".[1] Numerous publications have been devoted to potential applications of porphyrins in medicine as phototherapeutic agents[2] and in material sciences, e.g., as molecular wires.[3] It is therefore not surprising to witness a rapid development of synthetic efforts aimed at producing porphyrinlike molecules, designed to possess specific properties. Porphycene—the first known isomer of porphyrin—was obtained a decade ago.[4] The synthesis of this novel chromophore was followed by spectral studies involving various methods of molecular spectroscopy.[5−21] Comparison of the spectral, photophysical, and photochemical characteristics of porphyrin and porphycene reveals both analogies and variances. While the general spectral pattern is similar in the two compounds, significant differences are found regarding, e.g., intensities of electronic transitions, energy separation between excited states, the rates of the excited-state deactivation channels, and the behavior of the central protons.

For porphyrins, there have been many investigations in the field of vibrational and vibronic spectroscopy,[22−45] and the problems of interpretation of the vibrational spectra have been, in principle, resolved. For porphycenes, the corresponding studies are just beginning to emerge; however, the interpretation of vibrational structure is still lacking. Electronic absorption and fluorescence spectra of parent porphycene and its various derivatives have been recorded in liquid and glassy solutions,[13] where the vibronic structure was unresolved. In the same work, assignments of electronic states have been proposed on the basis of polarization and MCD measurements and the results of CNDO/S, INDO/S, and PPP calculations. Further spectral studies were aimed at the determination of transition moment directions by using the techniques of polarized spectroscopy.[16,17] These studies resulted in the discovery of a fast double-proton-transfer reaction occurring in the lowest excited singlet state. They also led to the conclusion that the dominant tautomeric species corresponds to the *trans* form, with the inner protons residing on opposite nitrogen atoms. A rapid tautomerization has been observed also in the ground state, using the solid-state [15]NMR measurements.[6] The results suggested that in the crystalline phase both *cis* and *trans* tautomers are present and that the tautomerization is fast on the NMR time scale, even at temperatures as low as 107 K. In a recent paper,[20] the experimental electronic spectra of porphycene in an argon matrix and the vibrational spectra in a nitrogen matrix and crystalline pellets were combined with the results of quantum chemical calculations of the vibrational pattern for both tautomeric structures. Since the calculations predicted a very similar pattern for both forms, the authors refrained from drawing a definite conclusion about the dominant species, even though the observation of a mutual exclusion principle in the Raman and IR spectra seems to favor the *trans* tautomer.

In this work, electronic spectra of porphycene (**1**) and 2,7,-12,17-tetrapropyl-*n*-porphycene (**2**) were investigated in low-temperature nitrogen and rare gas matrices. We also recorded high-resolution fluorescence spectra for **1** in isotropic rigid solutions using line-narrowing methods. The strategy was to obtain well-resolved spectra of these molecules in various media and to trace the influence of different matrices on the positions of different vibronic peaks. This was done in order to (i) assign the exact locations of the low-lying electronic transitions, (ii) obtain the vibrational frequencies in the S_0, S_1, and S_2 states, (iii) check the possibility of the existence of more than one tautomeric form, and (iv) compare the vibronic and site structure with the corresponding spectra of porphyrin (**3**).

* Corresponding author. E-mail waluk@ichf.edu.pl; Fax (+48) 391 20 238.
† Polish Academy of Sciences.
‡ Academy of Sciences of Belarus.
§ Institut für Organische Chemie der Universität.

CHART 1: Porphycene (1),
2,7,2,17-Tetra-*n*-propylporphycene (2), and Porphyrin (3)

1   **2**   R = n-C₃H₇   **3**
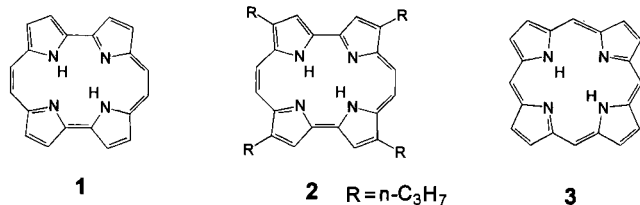
Experimental Section

The preparation of pure samples of some porphycenes and of parent porphyrin has been described elsewhere.[4a,b,46] The formulas are presented in Chart 1. Low-temperature matrices were produced by deposition on sapphire or quartz windows mounted onto the cold end (12 K) of a closed cycle two-stage Displex 202 (Air Products) refrigerator. The compounds were sublimed at 413−473 K in the stream of gas onto the cold substrate (background pressure 10^{-6} Torr). Typical matrix ratios were $1:10^4$ or lower. The gases used were N_2, Ar (both from Aldrich, 99.998+%), Kr, and Xe (both from Linde, 4.0).

Absorption spectra were recorded on a Shimadzu UV 3100 spectrophotometer. Emission was excited by an ILA 120 CW argon laser and monitored using a 1 m GDM 1000 double monochromator. The signal was recorded using a cooled Hamamatsu TE332RF photomultiplier.

The fluorescence line narrowing (FLN) technique for molecules in isotropic host media was applied for **1**. The method is based on selective laser excitation within the absorption band of the 0−0 electronic transition for the sample kept at liquid helium temperature. Under such conditions the fluorescence spectra consist of narrow zero-phonon lines, and the difference in frequencies between these lines and the line of excitation is equal to the frequency of the corresponding vibration in the ground state.[47]

For FLN spectra a tetrahydrofuran−toluene mixture (3:1) was used as a host glassy matrix. The measurements were performed on samples immersed into liquid helium in the optical cryostat. The spectra were measured with a DFS-24 spectrometer (0.8 m). A pulsed tunable dye laser (repetition rate 20 Hz, half-width of the generated band <0.1 nm, tuning region of 540−650 nm) pumped by an ILGI-504 nitrogen laser was used for the excitation of fluorescence. The data were acquired by a boxcar integrator coupled to a PC.

Results and Discussion

Spectra of Porphycenes in Different Matrices. Figure 1 presents the absorption spectra of **1** in nitrogen, argon, krypton, and xenon matrices. The fluorescence spectra of **1** in nitrogen and xenon matrices are shown in Figure 2. The vibrational frequencies extracted from the absorption and emission spectra are provided in Tables 1 and 2. The absorption spectra of **2** in nitrogen, argon, and krypton matrices are presented in Figure 3.

Figures 1−3 reveal inhomogeneous broadening of the peaks. For **1** and **2** (in contrast to **3**[37,38]) we observe mostly bands without site structure. Only for **1** on a sapphire window can one see a set of four sharp lines with half-widths of 6−10 cm^{-1}. For porphycene in a krypton matrix we observe the lines with a half-width of about 17 cm^{-1}. In xenon and nitrogen matrices the spectra are broader and consist of lines with half-widths of about 40 cm^{-1}. For **2,** spectral resolution is inferior in the same matrices. The presence of four propyl substitutents gives rise

to either stronger or less uniform interaction with the matrix and, thus, to spectral broadening. For more detailed information about vibrational structure, the use of line-narrowing techniques in fluorescence and fluorescence excitation spectra can be of great help, as has been recently observed for **1** in nitrogen matrices.[48] Such work is now in progress. Here we show (Figure 4) only the fluorescence spectrum of **1** in an isotropic medium (toluene/tetrahydrofuran 1:3 glass), obtained with the use of line-narrowing techniques.

Figure 5 shows the absorption spectra of **3** in argon and nitrogen matrices. The data from this picture will be used for comparison with the data for **1**.

Localization of the $S_2 \leftarrow S_0$ Electronic Transition. It is well-known for **3** that the $S_2 \leftarrow S_0$ electronic transition lies outside the region of the vibronic structure of the $S_1 \leftarrow S_0$ transition. The origin of the $S_2 \leftarrow S_0$ electronic transition is localized around 513 nm (near 19 500 cm^{-1}) and polarized perpendicularly to the long-wave $S_1 \leftarrow S_0$ electronic transition, with the origin at 613 nm (near 16 300 cm^{-1}). For **1,** the situation is different. The two transitions lie much closer in energy, which was suggested on the basis of the MCD measurements and was also predicted by theory.[13] At the same time, the polarization of the $S_2 \leftarrow S_0$ electronic transition in porphycenes is nearly perpendicular to that of the long-wave $S_1 \leftarrow S_0$ electronic transition, analogously to the situation in **3**.[16,17]

Based on different spectral shifts of vibronic lines belonging to transitions to the two states, the present results permit a detailed assignment of the second excited singlet state. We assign the origin of the $S_2 \leftarrow S_0$ electronic transitions in the absorption spectrum of **1** at 16 894 cm^{-1} (in the case of nitrogen matrix), which is 882 cm^{-1} higher than the 0−0 position of the $S_1 \leftarrow S_0$ electronic transition. The situation for **2** is very similar: The 0−0 position of the $S_2 \leftarrow S_0$ transition is observed at 16 784 cm^{-1} in the nitrogen matrix, and the shift from the $S_1 \leftarrow S_0$ electronic transition is practically the same as for **1**, 879 cm^{-1}. Such assignment is confirmed by the emission experiments and the spectral data for **2**. Comparison of the absorption and fluorescence spectra reveals the absence of intense lines with frequencies near 900 cm^{-1} in the fluorescence spectra of compounds **1** and **2**. A low-intensity emission band with frequency of 859 cm^{-1} (for **1**) does not correspond to the above-mentioned absorption line lying 894 cm^{-1} higher than the origin of the $S_1 \leftarrow S_0$ transition. This is clear from the comparison of the absorption and fluorescence spectra in nitrogen and xenon matrices. In fluorescence, practically the same frequency is observed for this mode in the two media (859 and 863 cm^{-1}, respectively), whereas in absorption, the shifts from the $S_1(0−0)$ band are very different (882 vs 838 cm^{-1}). Our conclusion about the localization of the $S_2 \leftarrow S_0$ electronic transition in the absorption spectrum of **1** and **2** is in agreement with previous observations.[13,20]

The matrix shifts of the S_1 and S_2 levels in **1** and **2** are comparable in magnitude, about 200 cm^{-1} to the red upon changing from argon or nitrogen to xenon. This reflects the observation that the intensities of both transitions are also similar, a situation very much different from that observed in **3**, where the oscillator strengths corresponding to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions differ by about an order of magnitude, the latter being much stronger (Figure 5).

It is interesting to note that the absorption spectra of **1** and **2** reveal large differences in the intensities of vibronic bands (cf. Figures 1 and 3). For compound **2** the activity of most bands is very low. For example, the bands with frequencies of 335,
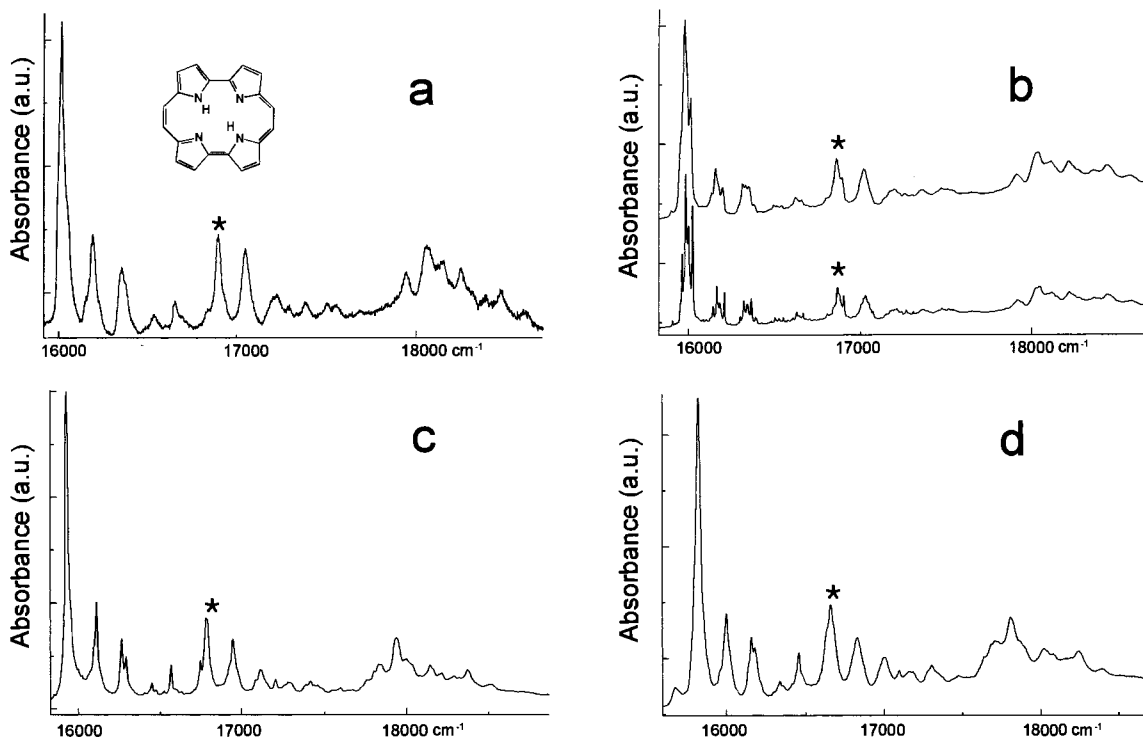
Porphycenes in Rare Gas and N Matrices

J. Phys. Chem. A, Vol. 102, No. 49, 1998 **10001**

Figure 1. Absorption spectra of **1** in nitrogen (a), argon (b), krypton (c), and xenon (d) matrices at 15 K. The spectra in argon are given for both quartz (top) and sapphire (bottom) windows; all other curves were recorded on a sapphire support. The asterisks mark the origin of the $S_2 \leftarrow S_0$ transition.
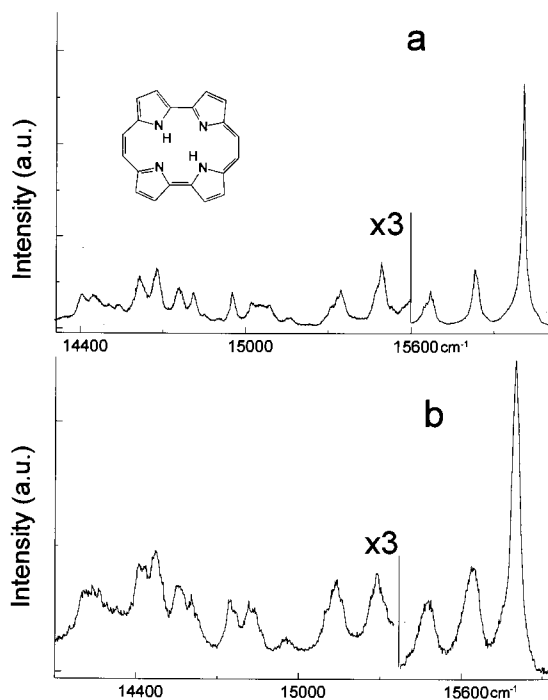

Figure 2. Fluorescence spectra of **1** in nitrogen (a) and xenon (b) matrices at 15 K. The emission was excited with the 514.5 nm line of the Ar laser.

363, and 637 cm^{-1} (in Kr matrix) are intense in the absorption spectra of **1** and weak in the spectrum of **2**. The reason for this difference is not clear. One can speculate that it is connected with the interaction of propyl substituents with the chromophore and the lowering of symmetry in **2** in relation to **1**. This problem requires theoretical calculations of the relative intensities in the absorption spectra of molecules **1** and **2**. A plausible explanation can be given for the region around 1050 cm^{-1} from the 0−0 transitions. It is well-known from the normal-coordinate analysis and the deuterium-exchange experiments that in **3** the normal modes with frequencies near 1050 cm^{-1} have large contributions from the protons attached to C_β atoms. If we assume a similar situation in porphycene, smaller intensity of the corresponding bands in **2** could be due to the fact that in this molecule there are 2 times less C_β protons than in **1**. One should also notice that in porphycene the two C_β protons on each pyrrolic ring are not equivalent.

Vibronic Structure of the S_0−S_1 and S_0−S_2 Electronic Transitions. The vibronic peaks observed in the absorption spectra of **1** in four different matrices are listed in Table 1. Contrary to the case of **3**, where the $S_1 \leftarrow S_0$ (Q_x) and $S_2 \leftarrow S_0$ (Q_y) electronic transitions are separated by more than 3000 cm^{-1}, vibronic manifolds of S_1 and S_2 interfere with each other in **1** and **2**, in particular in the region between 16 600 and 17 500 cm^{-1}. However, taking advantage of different matrix shifts observed for the two electronic transitions, it was possible to separate the vibronic components of the S_1 and S_2 manifolds. Another criterion was the comparison of the vibrational frequencies assigned to S_1 with those for the ground state obtained from fluorescence spectra. Most of the frequencies active in the emission (Table 2) have their counterparts in S_1; the changes in frequencies are rather small.

Without theoretical calculations of frequencies and forms of vibrations (normal-coordinate analysis) it is difficult to characterize the normal modes that are active in the spectra. Still, it is natural to look for some correspondence between the vibrational states of porphycenes and porphyrins. It is well-known that in **3**, which is of D_{2h} symmetry, the transition moments of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ are orthogonal. The former lies in the molecular plane and is parallel to the NH−HN direction; the latter, also lying in the molecular plane, is perpendicular to the NH−HN axis. The peaks observed in the spectra correspond to either totally symmetric vibrations (a_g

TABLE 1: Vibrational Frequencies (in cm⁻¹) Obtained from the Absorption Spectra of 1 at 15 K in Different Matrices[a]

N₂ 16 012 cm⁻¹	Ar 15 984 cm⁻¹	Kr 15 931 cm⁻¹	Xe 15 821 cm⁻¹	assign
141	140 sh	142 sh	137 sh	S₁
178	181	181	179	S₁
341	338	335	337	S₁
362	360	363	360	S₁
478 sh	478 sh	480	478	S₁
521	517	518	515	S₁
	538	546	536	S₁
592	591	594	594	S₁
638	640	637	633	S₁
		662	657sh	S₁
677	677			S₁
	695	699	698	S₁
725	717	730	728	S₁
822	821	815	811	S₁
882 (16894)	880 (16864)	851 (16782)	838 (16659)	origin of S₂←S₀
		993 sh (142)	981 sh (143)	S₂
1037 (155)	1046 (166)	1015 (164)	1006 (168)	S₂
	1168	1160		S₁
1193	1194			S₁
1212 (330)	1212 (332)	1185 (334)	1180 (342)	S₂
	1252 (372)	1219 sh (368)		S₂
1277	1282	1277	1273	S₁
1322	1323	1323 sh	.	S₁
1369 (487)		1332 (481)		S₂
	1382 (502)	1356 (505)	1343 (505)	S₂
		1369 (518)	1360 (522)	S₂
1488	1488	1487	1482	S₁
1535	1531	1529	1526	S₁
	1560	1558	1553	S₁
1671	1671	1665	1659	S₁
		1742 (891)	1731 (893)	S₂
		1826	1821	
		1869	1864	
1929 (1047)	1939 (1059)	1901 (1050)	1889 (1051)	S₂
		1917 (1066)	1911 (1073)	S₂
2045 (1163)	2046 (1166)	2005 (1154)	1988 (1150)	S₂
		2068 (1217)	2050 (1212)	S₂
2138 (1256)	2135 (1255)	2102 (1251)	2079 (1241)	S₂
2234 (1352)	2240 (1360)	2208 (1357)	2202 (1364)	S₂
		2228 (1377)		
2298 (1416)	2298 (1418)	2277 (1426)	2254 (1416)	S₂
2379 (1497)	2388 (1508)	2356 (1506)	2344 (1506)	S₂
		2387 (1536)	2376 (1538)	S₂
2462 (1580)	2466 (1586)	2439 (1588)	2424 (1586)	S₂
2602 (1720)	2603 (1723)	2584 (1733)	2570 (1732)	S₂
		3052	3052	S₁

[a] Peak positions are given relative to the 0−0 transitions of which the frequencies are given at the head of each column. The numbers in parentheses are given for transitions that were assigned to the S₂ manifold.

TABLE 2: Vibrational Frequencies (in cm⁻¹) in the Ground State of 1 Obtained from the Fluorescence Spectra of 1 at 15 K in Different Gas Matrices and at 4.2 K in a Tetrahydrofuran−Toluene Mixture[a]

N₂ 16 012 cm⁻¹	Ar 15 984 cm⁻¹	Kr 15 931 cm⁻¹	Xe 15 821 cm⁻¹	FLN[b] 15 920 cm⁻¹
				147
184	182	185	184	185
344	346	343	336	344
362	358	360	358	368
487	487			485
524	521	511	510	
535	538	527	538	530
556				553
668	672	669	665	666
683			686	690
698		698	703	711
		731	723	735
859	858	855	863	856
927	930	933		
961	957	963	961	968
1006	987	1010	1010	992
1063	1055	1061	1079	1075
1110				1122
1161	1166	1160	1203	1163
1204	1203	1201	1220	1203
1258	1253	1257	1265	1258
1336	1336	1336	1354	1332
1398	1399	1400	1395	1399
1472	1475	1470	1497	1472
1568	1540	1545	1562	1542
1568	1561	1569	1585	1563
1609	1610	1614	1614	1610

[a] Peak positions are given relative to the 0−0 transition of which the frequency is given at the head of each column. [b] Tetrahydrofuran/toluene (3:1).

the former is directed along the two NH nitrogen atoms, and the latter is close to being perpendicular to that direction. It is interesting to ask whether this qualitative similarity is also reflected in the vibronic structures of **1** and **3**.

Indeed, Figure 1 demonstrates that in the absorption spectrum of **1** the activities of vibrational transitions are very different for the S₁ and S₂ manifolds. The bands with frequencies of 178, 341, 362, and 638 cm⁻¹ (N₂ matrix) are most active in the S₁ absorption. From a general view of the S₁ absorption spectrum of **1** (a highly intense 0−0 transition) and the Franck−Condon principle, one could assume that the totally symmetric vibrations with similar polarization as the S₀ ← S₁ electronic transition moment will be more active in the spectrum. For the S₂ state, the situation is different. Much higher activity is observed for the modes with energies above 1000 cm⁻¹. This spectral behavior is qualitatively similar to that observed in **3**, and it is tempting to treat at least some of the higher frequency S₂ vibrations of **1** as formal analogues of the non-totally symmetric modes of porphyrin.

Some bands in the S₀, S₁, and S₂ states (e.g., the 1063 cm⁻¹ peak observed in the ground state of **1** in a nitrogen matrix and its counterparts in other matrices (Table 2)) are sensitive to the type of matrix. This may be connected with the interaction of the matrix with the embedded molecule and, possibly, with some change in the form of vibrations. The "matrix-sensitive" lines most probably correspond to vibrations with essential participation of C_β-hydrogen atoms; for such vibrations one can expect stronger interactions with the matrix. To trace the influence of the matrix in more detail, line-narrowing techniques should be of great help. Such investigations are now in progress.[48]

Possibility of Different Tautomeric Forms. The problem of the existence of possible two tautomeric forms of **1** has not

symmetry) or non-totally symmetric modes (b₁g species). The relative intensities of the bands corresponding to the two species are different in the two states: in general, the b₁g vibrations are more pronounced in S₂. For instance, in Q_x a strong band at 304 cm⁻¹ corresponding to an a_g vibration is followed by a weak one of b₁g symmetry at 411 cm⁻¹.[25,38] In Q_y, the intensities are reversed. Another illustration of the same trend is provided by the peaks at 710 (a_g) and 781 cm⁻¹ (b₁g) (for Q_x; in Q_y these frequencies become 711 and 768 cm⁻¹, respectively).

The lower symmetry of the *trans* tautomers of porphycene, C_{2h}, implies that all the ππ* transitions are of the same symmetry, B_u, and can be polarized in any direction lying in the molecular plane. However, the polarization studies of **1** and **2** reveal that these molecules have the S₁ and S₂ transition moments positioned qualitatively similar to the situation in **3**:[16,17]

Porphycenes in Rare Gas and N Matrices

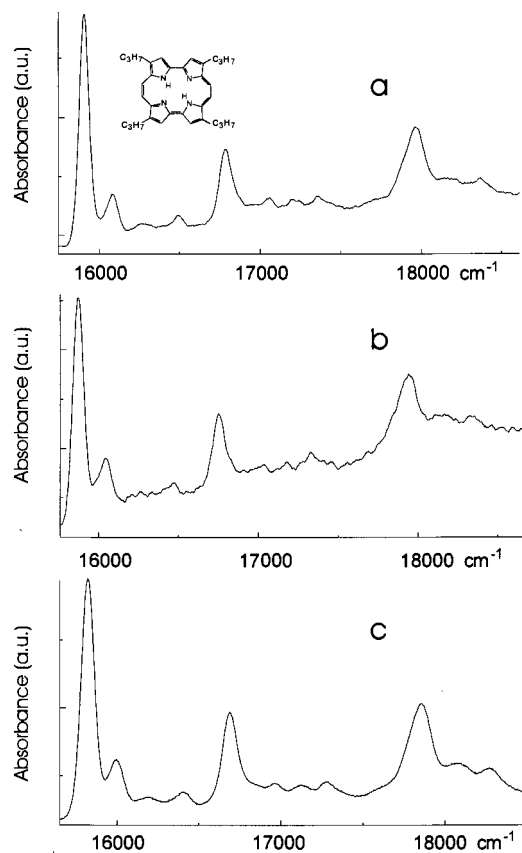*J. Phys. Chem. A, Vol. 102, No. 49, 1998* **10003**

Figure 3. Absorption spectra of **2** in nitrogen (a), argon (b), and krypton (c) matrices at 15 K.
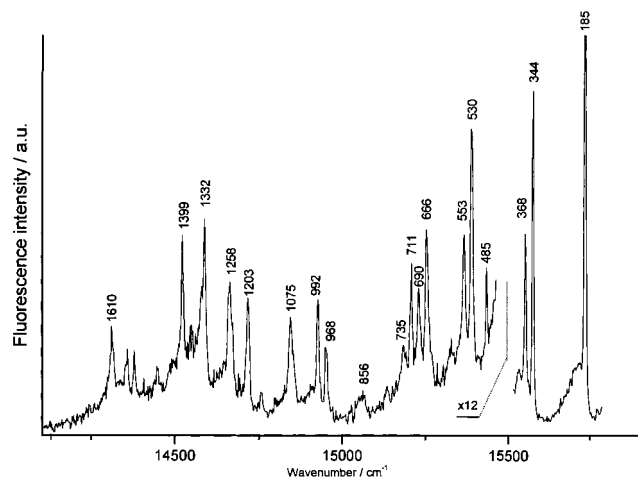

Figure 4. Fluorescence spectrum of **1** a glassy tetrahydrofuran−toluene (3:1) matrix at 4.2 K. The excitation was at 15 920 cm^{-1}.

yet been solved. The ^{15}N NMR data in the crystal point to the presence of four different species, pairwise interconverting on the time scale of the NMR experiment.[6] They have been assigned to *trans* and *cis* tautomers, the double degeneracy of each pair lifted by the intermolecular interactions in the crystal. In solutions, however, the *trans* form dominates, although a fraction of *cis* tautomers cannot be excluded.[13,17]

Our matrix data can be interpreted on the assumption that only one form, most probably the *trans*, is present. The spectra taken in various matrices do not differ much in the relative intensities and positions of the peaks, as should have been the case if two species differing in polarity were present (the *cis* forms should have a dipole moment, the *trans* should not). Even though some peaks are observed that, upon changing the matrix,
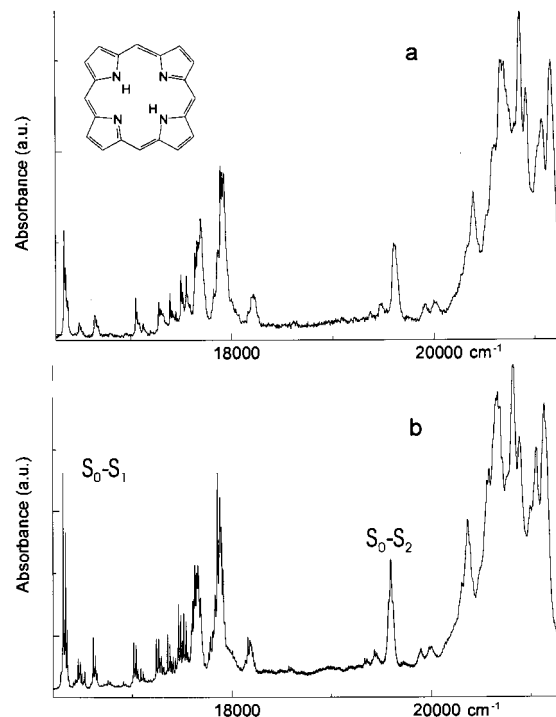

Figure 5. Absorption spectra of **3** in nitrogen (a) and argon (b) matrices at 15 K.

are shifted in a less regular way than observed for the majority of the peaks belonging to S_1 and S_2 manifolds, it seems safer to assign them to matrix-sensitive modes of the *trans* form rather than to the *cis* structure. Still, the problem requires further studies, certainly with better spectral resolution.

Our data confirm that the tautomerization in porphycene can be fast even at low temperatures. It is known that narrow-band irradiation of cryogenic solutions of **3** leads to hole burning due to phototautomerization.[31] Thus, the intensity of selectively excited fluorescence of porphyrin decreases in time, because of the depletion of the pumped site. In similar experiments performed on the sample of **1** at 4.2 K, we did not observe changes of fluorescence intensity. This may mean that either (i) there is no photoinduced proton transfer or (ii) the photo-tautomerization occurs, but is followed by a rapid back proton transfer. Our previous work on glassy solution of **1** and **2**[13,16,17] points to the latter possibility. The much faster tautomerization rate in porphycenes than in porphyrin is compatible with the finding that the internal NH−N hydrogen bonds are much stronger in the former.[4a]

Differences in Site Structure with Respect to the Spectra of Porphyrin. As already mentioned, the spectra of **1** are much less rich in site structure than those of **3**. Some similarities are observed in lighter matrices, in particular in argon, where, on the sapphire support, the vibronic lines of the S_1 manifold are split into quadruplets. However, in krypton and xenon matrices, only one main component is observed for **1**. This is in contrast to **3**, where the lines are split into doublets corresponding to the different orientations of the inner protons with respect to the environment. This has been established by showing that the components of the doublet may be transformed into each other upon selective optical pumping. The phototransformation is due to the photoinduced double proton transfer and corre-sponds to a pseudorotation of **3** by 90° about the axis perpendicular to the molecular plane.[36,37] Thus, the transition moment directions of the same electronic transition in the components of the doublet are orthogonal. This leads to
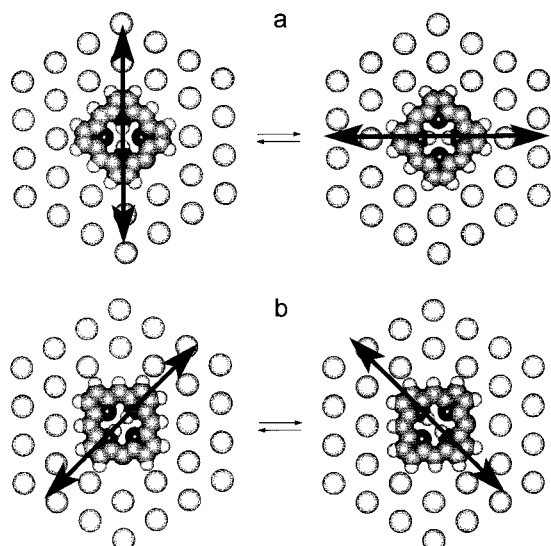
Figure 6. Representation of **3** incorporated into a xenon matrix, for two different orientations with respect to the matrix cage (a and b). For each situation, a pair of interconverting tautomers is shown, along with the transition moment direction corresponding to the $S_1 \leftarrow S_0$ transition.

different interaction with the anisotropic environment and, in consequence, to different transition energies. The splitting of the doublet lines in xenon is quite large, above 90 cm^{-1} in both absorption and emission spectra.[38,39]

It should be noted that a splitting of such magnitude could have easily been detected in our spectra, even though the line widths are larger than in the case of **3**. The absence of the splitting (or, at most, a much lower value, smaller than the line width, 17 cm^{-1} in krypton and <40 cm^{-1} in Xe) means that the difference in interaction energy with the matrix in the two *trans* forms of **1** is much smaller than in **3**.

To explain this finding, we first note that the lower symmetry of **1** implies that the transition moments in the two forms need no longer be orthogonal. However, from the fluorescence anisotropy data it is known that, for instance, for the S_0-S_1 transition this angle should be around 60°−80° and thus quite close to the value observed in **3**. What may be much more important is the relative orientation of the transition moment with respect to the matrix in each of the two forms. Here, a large difference between **1** and **3** can be expected. Let us consider possible arrangements of porphycene and porphyrin in a xenon matrix. Both molecules have very similar dimensions and shape. Substitutional replacement requires that at least seven xenon atoms be removed from the fcc crystal lattice[49] in order to accommodate **1** or **3**. This creates a hexagonal cavity, into which a molecule has to be inserted. Both **1** and **3** can be well represented by rectangles, the latter closer to a square. Several symmetrical ways of placing such a rectangle within a hexagonal cavity can be envisaged. One of them is presented in Figure 6a for porphyrin. It is easy to recognize that, for such an arrangement, the nearest xenon atoms are not located equivalently with respect to the two pairs of the opposite pyrrolic rings. It is clear that, for such a situation, two *trans* tautomeric forms of **3** will interact differently with the matrix.

Another arrangement, illustrated in Figure 6b, is obtained after rotating the molecule by 45° with respect to the previous case. Now, the two trans tautomers are equivalent with respect to their interaction with the environment, and no spectral splittings are to be expected.
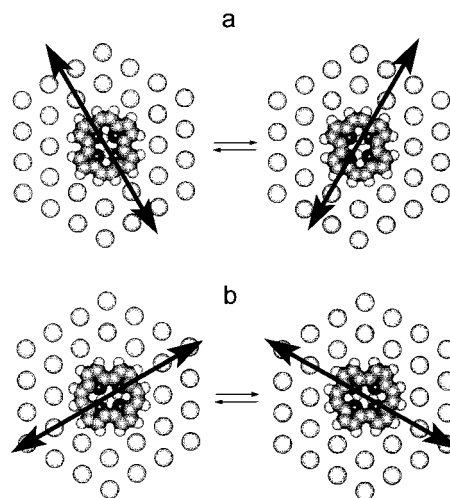

Figure 7. Representation of **1** incorporated into a xenon matrix, for two different orientations with respect to the matrix cage (a and b). See caption to Figure 6 for details.

The electronic spectra of **3** in xenon matrices do indeed show the presence of such two types of sites. Besides the most intense doublet, with the spacing of 90 cm^{-1}, another site, labeled X, of much weaker intensity, is observed.[38] Upon phototransformation, its spectral position changes very little, at most 2−3 cm^{-1}. It may not be accidental that the spectral position of this site in the $S_1 \leftarrow S_0$ transition is between the two lines of the main doublet. It is tempting to assign the main doublet to the situation depicted in Figure 6a, while the other site would correspond to the case of Figure 6b.

The same considerations applied to porphycene lead to completely different conclusions regarding site splitting. Figure 7a,b presents two ways of inserting **1** into a xenon crystal in a way analogous to that depicted in Figure 6a. In contrast to the case of **3**, no site splitting due to proton transfer is now to be expected. The reason is a different symmetry of the two chromophores, which dictates a different behavior of the transition moment directions after double proton transfer. In **3**, the transition moments are rotated by 90° from a position parallel or perpendicular to the long axis of the hexagonal cavity. In **1**, they are reflected in the plane perpendicular to the chromophore and containing the long axis of the hexagonal cavity. While the former transformation may lead to different energies of interaction with the matrix in the two tautomers, the latter may not.

We thus conclude that even though the two molecules may be located in a matrix in a very similar fashion, very different patterns of the site splittings may be observed. The differences are to be expected not only for xenon but also for krypton matrices, because krypton atoms are still large enough[50] to allow the placement of **1** or **3** in a cavity in a same way as that discussed for xenon. Indeed, while our spectra of **1** in krypton reveal narrow lines without site structure, significant splittings have been observed for **3**.[38] In lighter matrices, consisting of smaller atoms, the situation seems more complicated. More matrix atoms have to be taken out in order to accommodate the chromophore. Usually, this can be done in several ways, creating cages of different, nonregular shapes. Multiple sites are to be expected, and the structural differences between **1** and **3**, not crucial in larger matrices, can now be important. Still, a general prediction can be made regarding the differences in the site splitting pattern of the Q_x and Q_y bands in the two molecules. In **3**, the NH−HN direction and the in-plane direction perpendicular to it coincide with the symmetry axes

Porphycenes in Rare Gas and N Matrices

J. Phys. Chem. A, Vol. 102, No. 49, 1998 **10005**

and with the transition moments corresponding to Q_x and Q_y. It is thus natural to expect that the splitting patterns will be reversed for the two states. This is indeed observed for porphyrin: the lower energy component of the doublet in S_1 becomes the higher one in S_2, and vice versa.[38] In porphycene, on the other hand, the transition moments directions corresponding to Q_x and Q_y roughly bisect the long and short in-plane axes. Thus, in a pair of tautomers interconverting via double proton transfer, two possible transition moment directions corresponding to $S_1 \leftarrow S_0$ and two possible directions corresponding to $S_2 \leftarrow S_0$ are similarly oriented in space. In consequence, one should not expect large differences in the site-splitting patterns for the two lowest excited states, also because the intensities of both transitions are comparable. This is confirmed by the observation that the multiplet patterns which we observe for **1** in Ar are very similar for both $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions.

One should note that the differences in the site-splitting pattern between **1** and **3** should be revealed not only in the electronic but also in the IR spectra. The doublet splittings have been observed in the IR spectra of **3** in xenon and krypton matrices and correlated with the splittings in the electronic spectra.[37] The sign and amount of the splitting for each particular vibrational band is very important, since it may yield information about the form of the corresponding vibration. For porphycene, however, such splittings should be much weaker and more difficult to observe.

Summary and Conclusions

Application of matrix isolation spectroscopy techniques to porphycene and its tetrapropyl derivative allowed us to obtain the exact locations of the origins of the S_1 and S_2 electronic transitions. The two transitions lie much closer to each other than in porphyrin. In contrast to porphyrin, the intensity of both transitions is similar. The vibronic structures are different for the S_1 and S_2 manifolds and qualitatively similar to those observed in porphyrin.

No evidence has been obtained that would point to the presence of another tautomeric form, the *cis* structure.

Comparison of the spectral features observed in the highly resolved electronic spectra of porphyrin and porphycene led us to propose a model that accounts for the lack of site structure in the spectra of porphycene taken in xenon and krypton matrices. Albeit very approximate, this two-dimensional approach points to experiments that can further check its validity. For instance, the model predicts similar site structure patterns for **3** and for its derivatives in which the two inner protons are replaced by a metal atom. Indeed, our recent work shows close similarities between the matrix spectra of free base and metalloporphyrins.[41] On the other hand, the matrix spectra of metalloporphycenes are expected to be very different from the spectra of the free base. Actually, the site splittings in metalloporphycenes can be predicted to resemble those of porphyrin. This should be the effect of different symmetries of free base and metalloporphycene chromophores and, accordingly, of different directions of the transition moments with respect to the molecular skeleton: metalation of porphycene changes the symmetry from C_{2h} in the free base to D_{2h} in the metal derivative.

References and Notes

(1) Battersby, A. R.; Fookes, C. J. R.; Matcham, G. W. J.; McDonald, E. *Nature (London)* **1980**, *285*.

(2) (a) Kessel, D., Dougherty, T., Eds. *Porphyrin Photosensitization, Advances in Experimental Medicine and Biology 160*; Plenum: New York, 1983. (b) Andreoni, A., Cubeddo, R., Eds. *Porphyrins in Tumor Phototherapy*; Plenum: New York, 1984. (c) Fukuda, H.; Casas, A.; Chueke. F.; Paredes, S. *Int. J. Biochem.* **1993**, *25*, 1395. (d) Hamblin, M.; Newman, E. J. *Photochem. Photobiol. B: Biol.* **1994**, *23*, 3. (e) Richert, C.; Wessels, J.; Müller, M.; Kisters, M.; Benninghaus, T.; Goetz, A. *J. Med. Chem.* **1994**, *37*, 2797. (f) Dolphin, D. *Can. J. Chem.* **1994**, *72*, 1005. (g) Meng, G. G.; James, B. R.; Skov, K. A.; Korbelik, M. *Can. J. Chem.* **1994**, *72*, 2447. (h) Bonnett, R. *Chem. Soc. Rev.* **1995**, 19. (i) Boyle, R. W.; Dolphin, D. *Photochem. Photobiol.* **1996**, *64*, 469.

(3) (a) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1996**, *68*, 1373. (b) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.

(4) (a) Vogel, E.; Kocher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *25*, 257. (b) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928. (c) Vogel, E.; Kocher, M.; Lex, J. *Isr. J. Chem.* **1989**, *29*, 257. (d) Vogel, E. *Pure Appl. Chem.* **1990**, *62*, 557. (e) Vogel, E.; Koch, P.; Hou, X.-L.; Lex, J.; Lausmann, M.; Kisters, M.; Aukauloo, M. A.; Richard, P.; Guilard, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1600. (f) Vogel, E. *Pure Appl. Chem.* **1993**, *65*, 143. (g) De Munno, G.; Lucchesini, F.; Neidlein, R. *Tetrahedron* **1993**, *49*, 6863. (h) Guilard, R.; Aukauloo, M. A.; Vogel, E. *Synthesis* **1995**, *12*, 1480. (i) Chang, C.-K.; Morrison, I.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1995**, *11*, 1173. (j) Nonell, S.; Bou, N.; Canete, M. *Tetrahedron Lett.* **1995**, *36*, 3405. (k) Che, C.-M.; Li, Z.-Y.; Peng, S.-M. *Inorg. Chem.* **1995**, *34*, 98. (l) Falk, H.; Chen, Q.-Q. *Monatsh. Chem.* **1996**, *127*, 69. (m) Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461. (n) Vogel, E. *Pure Appl. Chem.* **1996**, *68*, 1355. (o) Setsune, J.; Hazama, K. *Tetrahedron Lett.* **1997**, *38*, 2513.

(5) Aramendia, P. F.; Redmond, R. W.; Nonell, S.; Schuster, W.; Braslavsky, S. E.; Schaffner, K.; Vogel, E. *Photochem. Photobiol.* **1986**, *44*, 555.

(6) Wöhrle, B.; Limbach, H.-H.; Köcher, M.; Ermer, O.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 934.

(7) Ofir, H.; Regev, A.; Levanon, H.; Vogel, E.; Köcher, M.; Balci, M. *J. Phys. Chem.* **1987**, *91*, 2686.

(8) Levanon, H.; Toporowicz, M.; Ofir, H.; Fessenden, R. W.; Das, P. K.; Vogel, E.; Köcher, M.; Pramod, K. *J. Phys. Chem.* **1988**, *92*, 2429.

(9) Schlüpmann, J.; Huber, M.; Toporowicz, M.; Köcher, M.; Vogel, E.; Levanon, H.; Möbius, K. *J. Am. Chem. Soc.* **1988**, *110*, 8566.

(10) Redmond, R. W.; Valduga, G.; Nonell, S.; Braslavsky, S. E.; Schaffner, K. *J. Photochem. Photobiol. B: Biol.* **1989**, *3*, 193.

(11) Nonell, S.; Aramendia, P. F.; Heihoff, K.; Negri, R. M.; Braslavsky, S. E. *J. Phys. Chem.* **1990**, *94*, 5879.

(12) Schlupmann, J.; Huber, M.; Toporowicz, M.; Plato, M.; Köcher, M.; Vogel, E.; Levanon, H.; Möbius, K. *J. Am. Chem. Soc.* **1990**, *112*, 6463.

(13) Waluk, J.; Müller, M.; Swiderek, P.; Köcher, M.; Vogel, E.; Hohlneicher, G.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 5511.

(14) Gael', V. I.; Kuz'mitskii, V. A.; Solov'ev, K. N. *Dokl. Phys. Chem.* **1991**, *316*, 166.

(15) Bernard, C.; Gisselbrecht, J. P.; Gross, M.; Vogel, E.; Lausmann, M. *Inorg. Chem.* **1994**, *33*, 2393.

(16) Waluk, J.; Vogel, E. *J. Phys. Chem.* **1994**, *88*, 4530.

(17) Andersen, K. B.; Vogel, E.; Waluk, J. *Chem. Phys. Lett.* **1997**, *271*, 341.

(18) Sessler, J. L.; Brucker, E. A.; Lynch, V.; Choe, M.; Sorey, S.; Vogel, E. *Chem. Eur. J.* **1996**, *2*, 1527.

(19) Braslavsky, S. E.; Müller, M.; Mártire, D. O.; Pörtning, S.; Bertolotti, S. G.; Chakravorti, S.; Koç-Weier, G.; Knipp, B.; Schaffner, K. *J. Photochem. Photobiol. B* **1997**, *40*, 191.

(20) Malsch, K.; Hohlneicher, G. *J. Phys. Chem. A* **1997**, *101*, 8409.

(21) Malsch, K.; Roeb, M.; Karuth, V.; Hohlneicher, G. *Chem. Phys.* **1998**, *227*, 331.

(22) Plus, R.; Lutz, M. *Spectrosc. Lett.* **1974**, *7*, 133.

(23) Gladkov, L. L.; Gradyushko, A. T.; Solovyov, K. N.; Shulga, A. M.; Starukhin, A. S. *J. Mol. Struct.* **1978**, *47*, 463.

(24) Bykovskaya, L. A.; Gradyushko, A. T.; Personov, R. I.; Romanovskii, Y. V.; Solov'ev, K. N.; Starukhin, A. S.; Shulga, A. M. *J. Appl. Spectrosc.* **1978**, *29*, 10; 45.

(25) Bykovskaia, L. A.; Personov, R. I.; Romanovskii, U. V. *J. Appl. Spectrosc.* **1979**, *31*, 910.

(26) Gladkov, L. L.; Gradyushko, A. T.; Sivchik, V. V.; Solovyov, K. N. *J. Appl. Spectrosc.* **1984**, *40*, 275.

(27) Solovyov, K. N.; Gladkov, L. L.; Starukhin, A. S.; Shkirman, S. F. *Spectroscopy of Porphyrins: Vibrational States;* Nauka i Tekhnika: Minsk, 1985 (in Russian).

(28) Gladkov, L. L.; Starukhin, A. S.; Shulga, A. M. *Spectrochim. Acta A* **1987**, *43*, 1125.

(29) Völker, S.; Macfarlane, R. M.; Genack, A. Z.; Trommsdorff, H. P.; van der Waals, J. H. *J. Chem. Phys.* **1977**, *67*, 1759.

(30) Völker, S.; van der Waals, J. H. *Mol. Phys.* **1976**, *32*, 1703.

(31) Völker, S.; Macfarlane, *Chem. Phys. Lett.* **1979**, *61*, 421.

(32) Kim, B. F.; Bohandy, J. *J. Mol. Spectrosc.* **1978**, *73*, 332.

(33) Bohandy, J.; Kim, B. F. *Spectrochim. Acta A* **1980**, *36*, 463.

(34) Even, U.; Magen, J.; Jortner, J.; Friedman, J.; Levanon, H. *J. Chem. Phys.* **1982**, *77*, 4374.

(35) Even, U.; Jortner, J. *J. Chem. Phys.* **1982**, *77*, 4391.

(36) Radziszewski, J.; Burkhalter, F. A.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 61.

(37) Radziszewski, J.; Waluk, J.; Michl, J. *Chem. Phys.* **1989**, *136*, 165.

(38) Radziszewski, J.; Waluk, J.; Michl, J. *J. Mol. Spectrosc.* **1991**, *140*, 373.

(39) Radziszewski, J.; Waluk, J.; Nepraš, M.; Michl, J. *J. Phys. Chem.* **1991**, *95*, 1963.

(40) Radziszewski, J.; Nepraš, M.; Balaji, V.; Waluk, J.; Vogel, E.; Michl, J. *J. Phys. Chem.* **1995**, *99*, 14254.

(41) Starukhin, A.; Shulga, A.; Waluk, J. *Chem. Phys. Lett.* **1997**, *272*, 405.

(42) Li, X. Y.; Zgierski, M. Z. *J. Phys. Chem.* **1991**, *95*, 4268.

(43) Kozlowski, P. M.; Zgierski, M. Z.; Pulay, P. *Chem. Phys. Lett.* **1995**, *247*, 379.

(44) Kozlowski, P. M.; Jarzecki, A. A.; Pulay, P. *J. Phys. Chem.* **1996**, *100*, 7007.

(45) Kozlowski, P. M.; Jarzecki, A. A.; Pulay, P.; Li, X. Y.; Zgierski, M. Z. *J. Phys. Chem.* **1996**, *100*, 13985.

(46) Eisner, U.; Linstead, R. P. *J. Chem. Soc.* **1955**, *11*, 3749.

(47) Personov, R. I.; Al'shits, E. I.; Bykovskaia, L. A. *Opt. Commun.* **1972**, *6*, 169.

(48) Starukhin, A.; Sepioł, J.; Wild, U. P.; Waluk, J. Manuscript in preparation.

(49) Sears, D. R.; Klug, H. P. *J. Chem. Phys.* **1962**, *37*, 3002.

(50) Losee, D. L.; Simmons, R. O. *Phys. Rev.* **1968**, *172*, 944.