Fluorescence Excitation Spectroscopy of Octatetraene-Xe van der Waals Clusters

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Fluorescence excitation spectrum of the *trans,trans*-1,3,5,7-octatetraene(OT)-Xe van der Waals clusters formed in supersonic jet expansions has been obtained. The transition lines corresponding to the van der Waals clusters of OT with Xe are observed in the lower frequency side of the OT band origin. Based on the spectral shifts, fluorescence lifetimes, and concentration dependence of the peak intensities, most of the transition lines are assigned to the OT-Xe$_n$ (n = 1, 2, 3, 4) clusters. Long progressions of a van der Waals vibrational mode are observed for n = 1, 2, 3 and 4 clusters and assigned to rocking of the OT moiety with respect to the Xe atom with the help of *ab initio* quantum mechanical calculation.

Introduction

Studies on various van der Waals clusters have provided interaction potentials of the collision pairs of atom-atom, atom-molecule, or molecule-molecule, which have improved the understanding for the molecular interactions among the collision pairs and the solvation dynamics.[1,2] Since the rare gas atoms are the simplest molecules of all and thus interpretation of the experimental observations and theoretical calculations are less demanding, van der Waals clusters of the rare gas atoms with other molecules have been both intensively and extensively studied. High-resolution spectroscopic studies on the relatively small clusters like the atom-rare gas atom or diatomic molecule-rare gas atom(s) clusters have focused onto the spectral shifts, the changes of the lifetimes of the excited states, and geometries of the clusters. For the clusters of relatively large polyatomic molecules with rare gas atoms, the weak interactions between the chromophores in the polyatomic molecules and the rare gas atoms have been main topics of investigation.

Trans,trans-1,3,5,7-Octatetraene (OT) is a model molecule of linear polyenes which have a conjugated double bond structure, playing important roles in photobiological systems.
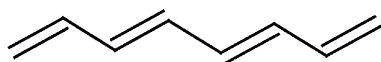
***trans, trans*-1,3,5,7-Octatetraene**

Conversion of light into chemical energy in plants and animals involves the photochemical transformation of the polyene chromophores such as carotenoids and retinals.[3] In the conversion process, the polyene chromophores are supposedly first excited to the electronically excited potential energy surface and undergo *cis-trans* isomerization on the excited potential energy surface.[4] The solvent molecules near the polyene chromophore may affect the isomerization on the excited potential surface via collisional relaxation and/or solvent reorganization. Therefore, the van der Waals clusters of the polyenes with rare gas atoms will be an excellent system to elucidate the interactions of the polyene chromophore with the solvent molecules, which are involved in the photochemical conversion of light in biological systems.

Some years ago, this group has reported the role of the rare gas atoms in the electronic relaxation of the electronically excited OT-rare gas clusters.[5] The heavy rare gas atoms attached to the OT molecule were found to enhance the electronic relaxation of OT through the external heavy atom effect. That is, the fluorescence lifetimes of the van der Waals clusters of OT with Xe atom(s) were measured to be significantly shorter than that of the bare OT molecule, while those with Ar atoms show no quenching of the excited OT. Kr clusters were located in between the Ar and Xe clusters.

As a continuing work, we report a spectroscopic investigation for the van der Waals clusters of the OT and one of the rare gases, Xe in this article. The spectral shifts, cluster size assignments, and frequencies of a van der Waals mode, resulting from the interaction between the polyene chromophore and rare gas atoms, are measured. Although the clusters with other rare gas atoms, Ar and Kr, had also been investigated, the spectra for these clusters are much more complicated and their interpretation requires extensive theoretical works, and thus the scope of this paper is limited only to the clusters with Xe.

Experimental Section

The experimental apparatus employed in this work is

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basically the same as reported previously.[5] The van der Waals clusters of *trans,trans*-1,3,5,7-octatetraene with the Xe atoms were synthesized by expanding the gas mixture containing the OT molecules and Xe gas seeded in He carrier gas into vacuum through a nozzle with a small orifice. A mixture of the He carrier gas and Xe gas was prepared in a stainless steel reservoir by mixing the pure He and the premixtures of Xe in He with the Xe concentration of about 5%. Solid octatetraene placed inside the nozzle maintained at 35 °C left sublimed into the mixture of the rare-gas and He carrier gas kept at a stagnation pressure of 2.5 atm, and the mixture was expanded through a pulsed valve (Newport BV100) with a 0.5 mm nozzle diameter. The output beam from a pulsed dye laser (Lambda Physik FL 3002) pumped with a XeCl excimer laser (Lambda Physik EMG 104MSC) crossed the supersonic jet of the clusters at 15 mm from the nozzle. Fluorescence from the excited OT and its van der Waals clusters was collected with a 2" diameter quartz lens, filtered with a color filter and an aperture, and then detected with a fast-response PMT (Hamamastu H3284) with about 300 ps risetime. Fluorescence excitation spectrum of the clusters was recorded from 344 to 347 nm, which correspond to the frequency region where the vibronic origin (O_{48}) band of the $S_1 \leftarrow S_0$ ($2^1A_g \leftarrow 1^1A_g$) transition appears.[6] The vibronic origin was observed at 29,024.9 cm^{-1}.[6] The energy of the excitation pulse was kept less than 500 μJ and the laser beam was weakly collimated to $\approx$ 2 mm diameter at the interaction region to avoid saturation of transitions. The optogalvanic spectrum of a Ne hollow cathode lamp provided a frequency calibration for the dye laser with an accuracy of $\pm$ 0.5 cm^{-1}.

Fluorescence lifetimes were recorded with a 500 MHz digital oscilloscope (LeCroy 7200) by averaging 500-1000 decay traces and stored in a floppy diskette in the built-in disk driver. The traces were then transfered to a personal computer and fit with a commercial least squares regression routine. The time resolution of the fluorescence lifetime measurements was limited by the 15 ns pulse duration of the excitation laser. Fitting the fluorescence decay profiles to single exponential gave the reported lifetimes.

The *trans,trans*-1,3,5,7-octatetraene sample was synthesized by dehydration of 2,4,8-octatrien-6-ol using pyridinium *p*-toluenesulfonate as a catalyst following the procedure described previously.[7] The alcohol was purchased from Sorl Laboratory in Japan and had a measured purity of 99.7% by HPLC. The crystalline sample of OT was stored in the nitrogen atomosphere at -80 °C before use in order to avoid polymerization.

The *ab initio* calculations were executed in a personal computer and an IBM RS 6000 workstation with the standard methods included in the Gaussian 98 for Windows and Gaussian 98 packages, respectively.[8]

Results and Discussion

When the Xe gas was added to the gas mixture for jet expansion, some weak peaks that may be attributed to the van der Waals clusters of the OT and Xe appeared at the lower frequencies of the O_{48} band of OT.[6] The fluorescence
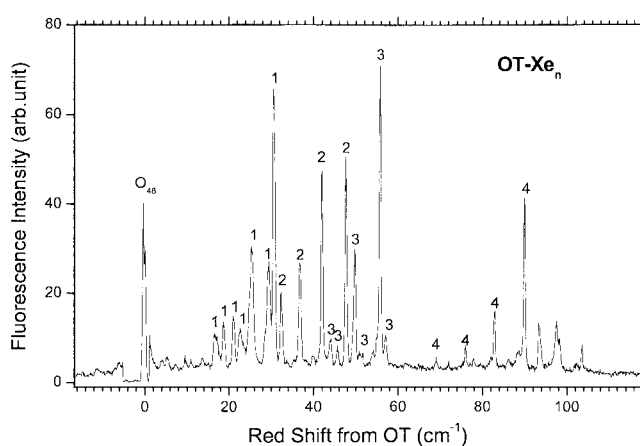

Figure 1. The fluorescence excitation (FE) spectrum of the OT-Xe$_n$ clusters. The PMT signal was decreased by a factor of 70-80 by decreasing the voltage applied to the PMT near the bare OT transition to avoid saturation. The numbers on top of each peak are the number of the Xe atoms in the clusters (see the text.).

excitation (FE) spectrum of the van der Waals clusters, which was taken at the 2.5 atm stagnation pressure and the 1.0% Xe concentration in He, is shown in Figure 1. Since the fluorescence signal from the bare OT excited to the vibronic origin (O_{48}) at 29,024.9 cm^{-1} was too strong compared to the weak transition lines of the clusters, the PMT voltage was decreased near the origin by 500 V to reduce the intensity to the appropriate level. No other wavelength region was scanned in search of van der Waals transitions because the OT molecule shows many weak peaks due to many low frequency vibrational modes except the region near the vibronic origin (O_{48}).[6]

By comparing the spectrum in Figure 1 with the FE spectrum of the bare OT, the transition lines corresponding to the van der Waals clusters were identified. Since no transition line of the bare OT molecule is expected at the lower frequency side to the vibronic origin (O_{48}), the van der Waals clusters of OT and Xe, OT-Xe$_n$ (*n* represents the number of the Xe atoms attached to OT.), are responsible for the all peaks observed in Figure 1 except the vibronic origin (O_{48}) of OT. The transition lines observed in Figure 1 are listed in Table 1 with the peak positions and intensities.

The first step in the analyses of the van der Waals clusters spectrum is to identify the number of the Xe atoms in the van der Waals clusters responsible for each peak. The best experimental method to assign the cluster size is the mass-selective multiphoton ionization spectroscopy. Since the ionization of the OT excited to the 2^1A_g excited state requires an additional photon near 200 nm[9] and the second tunable laser system for the 200 nm photon generation was not available in this laboratory, a less straightforward but quite frequently adopted method was employed in this work; the peak intensities are measured as a function of the Xe concentration in the carrier gas mixture.[10] The intensities of the transition lines of the clusters with the larger number of the Xe atoms should show stronger dependences on the Xe concentrations than the clusters with the smaller number of Xe.

Table 1. Positions of the observed peaks corresponding to the octatetraene-Xe$_n$ van der Waals clusters

Peak position[a] (cm^{-1})	Relative intensity[b]	Lifetime (ns)	Number of Xe atoms
0.00 (O$_{48}$ of OT)	N/A	320	0
16.5	15.7	59.2	1
18.7	19.2	63.2	1
21.0	21.2	62.2	1
22.7	17.3	64.4	1
25.3	43.2	62.4	1
29.4	38.2	58.4	1
30.6	92.7	60.0	1
32.3	29.3	49.3	2 (2+0)
36.7	37.9	50.7	2 (2+0)
41.9	68.1	48.2	2 (2+0)
44.0	14.0	38.3	3
45.6	11.7	40.7	3
47.6	71.4	48.7	2 (2+0)
49.7	42.2	37.6	3
55.8	100	39.0	3
57.0	15.0	40.4	3
69.0	4.3	45.1	4
75.9	8.7	36.7	4
82.9	22.7	35.6	4
86.2	4.5	–	
88.5	5.7	35.9	
89.9	58.5	29.8	4
93.3	15.7	44.4	
97.5	16.3	31.3	
98.2	5.0	36.7	
103.5	8.7	56.8	

[a]The red shift from the O$_{48}$ band of the *trans,trans*-1,3,5,7-octatetreaene.
[b]The relative intensity for the 55.8 cm^{-1} peak as 100.

Figure 2 shows the spectra measured at various Xe concentrations ranging from 1.0% to 0.08%. As the Xe concentration decreases, the peaks at larger spectral shifts, which are thought to be those of the larger clusters, fade out more rapidly. From the concentration dependence shown in Figure 2, all transition lines corresponding to OT-Xe$_n$ clusters in Figure 1 can be classified into 4 groups. The lines marked 1 on top of the peaks in Figure 1 persist even at the lowest concentration (0.08%) of Xe, which suggests that these correspond to the cluster of OT with a single Xe atom, *i.e.*, OT-Xe. The second group, which labeled with 2, shows the stronger dependence than the OT-Xe clusters but weaker than the others, must be the OT-Xe$_2$ clusters. The third group marked with 3 follows the second group and thus can be assigned to the OT-Xe$_3$ clusters. The last group, which shows the largest spectral shifts and labeled with 4, should be the OT-Xe$_4$. The unlabeled peaks located above 91 cm^{-1} are hardly assignable only from the concentration-dependent spectral changes, and thus the assignment for these peaks are reserved.

As reported previously,[5] the heavy Xe atoms residing near the OT molecule enhance the electronic relaxation of the electronically excited OT (S$_1$). Thus the fluorescence lifetimes of the OT-Xe$_n$ clusters are much shorter than that of the bare OT molecule. The lifetimes measured at each
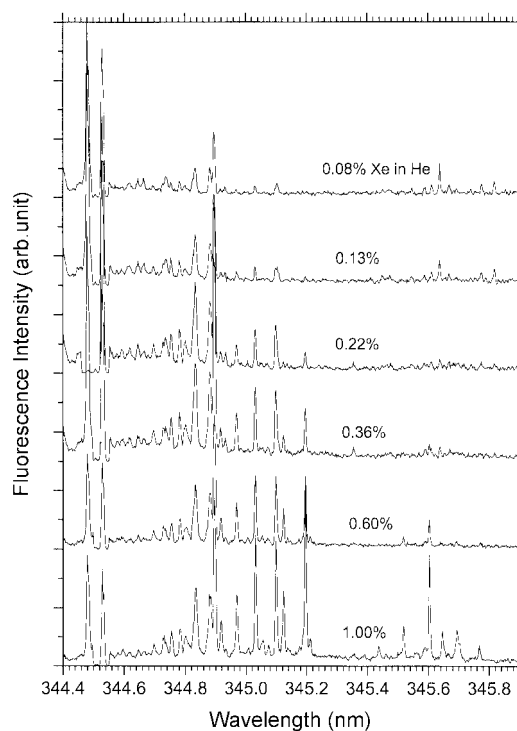

Figure 2. Concentration dependence of the FE spectrum of the OT-Xe$_n$ clusters. As the concentration of Xe decreases, the intensities of the peaks corresponding to larger clusters fade out more rapidly than the smaller ones.

labeled peak in Figure 1 are listed in Table 1 and shown in Figure 3.

The measured fluorescence lifetimes strongly support the cluster size assignment given above (see Figure 3). All the lines assigned to the OT-Xe clusters demonstrate the longest lifetimes grouped with a narrow dispersion and well separated from others. The lifetimes of the OT-Xe$_2$ clusters are located in between those of the OT-Xe and OT-Xe$_3$. Figure 3 shows
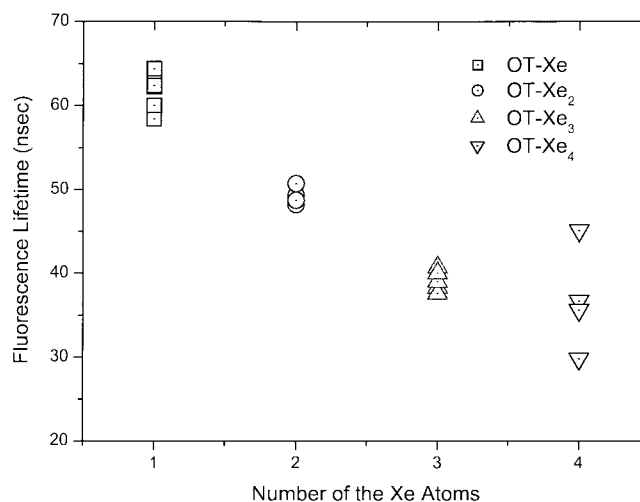

Figure 3. Fluorescence lifetimes of the OT-Xe$_n$ clusters. Except the $n = 4$ clusters, the lifetimes of the clusters with the same number of the Xe atoms are grouped with a narrow dispersion, confirming the size assignments.

that the lifetimes of the OT-Xe$_4$ clusters are less discernable from those of the OT-Xe$_3$ than others, but the peak positions that are far shifted red from the OT-Xe$_3$ confirm the assignment. As can be seen in Table 1, the lifetimes of the unassigned lines located red from the OT-Xe$_4$ are comparable to the OT-Xe$_4$ and also quite scattered, and thus do not help our assignment of these peaks.

It can be easily noticed in Figure 1 that the four transition lines corresponding to the OT-Xe$_2$ clusters are almost equally spaced. Such series of equally spaced lines are also noticeable for the OT-Xe, OT-Xe$_3$, and OT-Xe$_4$ clusters. These series of transition lines must be the progressions of a van der Waals vibrational mode of the clusters. The different conformers of a van der Waals cluster can give similar multiple transition lines, but the positions of the transition lines should not be so regular as observed in Figure 1. The vibrational level spacings measured from Figure 1 are summarized in Table 2 for the OT-Xe$_n$ (n = 1, 2, 3, 4) clusters. Table 2 demonstrates that the vibrational spacing steadily increases with the increase of the number of Xe atoms surrounding the OT molecule.

Ab initio calculation has demonstrated that *trans,trans*-1,3,5,7-Octatetraene is a planar molecule belonging to the

Table 2. Vibrational spacings of OT-Xe$_n$ clusters

	OT-Xe^a (cm^{-1})	OT-Xe$_2$ (cm^{-1})	OT-Xe$_3$ (cm^{-1})	OT-Xe$_4$ (cm^{-1})
$v=1 \leftrightarrow v=0$	5.3	5.7	6.1	7.0
$v=2 \leftrightarrow v=1$	4.3 6.6 (5.4$_5$)^b	5.2	5.8	7.0
$v=3 \leftrightarrow v=2$	–	4.4	4.1, 5.7	6.9

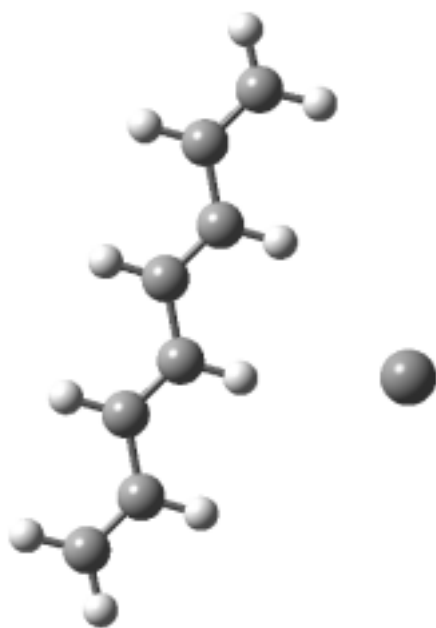^{a}For the dominant structural isomer. ^{b}The average value for the doublet.

Figure 4. The *ab initio* structure of the OT-Xe van der Waals cluster.

C$_{2h}$ point group.[11] As in the clusters of the planar molecules with fused benzene rings such as naphthalene, phenanthrene, tetracene, perylene,[12,13] and pentacene with rare gas atoms, it is expected that the Xe atom is located on top of the molecular plane of OT in OT-Xe. In contrast to our expectation, however, *ab initio* calculation shows that the geometries with the Xe atom on top of the OT plane are the transition states and that the geometry, in which the Xe atom is located in the same plane as the OT molecule as in Figure 4, is most stable.

In Figure 1, it can be noticed that there exist two band origins (29.4 and 30.6 cm^{-1} bands) for the OT-Xe clusters. The *ab initio* calculation at the HF/3-21G level provides a clue to understanding the observations. It predicts that the geometries with the Xe atom at the bays of the C$_1$-C$_2$-C$_3$ and C$_5$-C$_6$-C$_7$ correspond to the metastable local minima of which energies are very close. Hence there exist three isomers for the OT-Xe clusters, one of which is the one in Figure 4, having the lowest energy and the largest population. The other two are the metastable geometries mentioned above. These have nearly the same energies and thus render a single peak (a little broad one at 29.4 cm^{-1}) in the FE spectrum. They have higher energies than that of Figure 4 and lower populations as observed in the FE spectrum. A doublet structure at 18.7 and 21.0 cm^{-1} seems to originate from tunneling splitting of a vibrationally excited level. As shown in *ab initio* calculation, the OT-Xe cluster has a potential with multiple minima and such a doublet splitting can be anticipated. Since the exact potential is not known at this point, however, further discussion for the splitting is deferred.

For the OT-Xe$_2$ clusters, two isomeric structures, *i.e.*, two Xe atoms on one side (represented as (2 + 0)) and one Xe atom on each side (represented as (1 + 1)) are possible. Because the spectrum in Figure 1 and the size assignment given above demonstrate that there exists only one isomer of OT-Xe$_2$, it should be found out which isomer is responsible for the spectrum. If two Xe atoms in OT-Xe$_2$ are located on the other side of the molecule plane, the spectral shift should be nearly twice of that of OT-Xe as observed in many aromatic molecule-rare gas clusters.[12] The spectral shift of the origin band of the OT-Xe$_2$ is 47.6 cm^{-1}, which is much smaller than twice of that of OT-Xe, 30.6 cm^{-1}, suggesting that two Xe atoms are in the same side of the molecular plane. In terms of energetics, the structure with two Xe atoms on one side is also more favorable than the counter part since the Xe-Xe attraction further stabilizes the cluster.

For the OT-Xe$_3$ and OT-Xe$_4$ clusters, many more possible isomeric structures, which cannot be distinguished with only the spectral shifts, exist. An ultra high-resolution spectroscopy that resolves the rotational structure of the bands will confirm the structure assignments.

In the electronic spectroscopic studies on the polyatomic molecule-rare gas atom(s) van der Waals clusters, it is not common to observe long progressions involving the van der Waals vibrational mode. In the OT-Xe$_n$ clusters, exceptionally long progressions are observed as summarized in Table 2, especially in the OT-Xe$_2$ cluster. Such long progressions

Table 3. Low-frequency vibrational modes of OT-Xe obtained in *ab initio* calculation[a]

Modes	Harmonic frequencies (cm^{-1})	Approximate motion
v_{49}	19.8	
v_{50}	16.5	
v_{51}	6.2	Rocking of the OT moiety with respect to the Xe atom

[a]HF/3-21G.

appear when a large structural change takes place while excitation. In Table 3, the low-frequency vibrational modes that are obtained in *ab initio* calculation are summarized with their atomic motions. Since the frequency of the lowest frequency mode (v_{51}) is very close to that observed in this work and all others are quite far from it, we assigned the observed low-frequency progressions to v_{51}. The vectorial representation in Figure 5 shows that the v_{51} mode is the rocking of the OT moiety with respect to the Xe atom.

Now it is requird to answer to the question why the v_{51} mode is active in the $S_1 \leftarrow S_0$ ($2^1A_g \leftarrow 1^1A_g$) transition. It is well known that the bond orders in the OT molecule invert upon the $S_1 \leftarrow S_0$ excitation.[11] That is, the double bonds in the S_0 (1^1A_g) state become almost single bonds and *vice versa*. Due to the so-called bond order inversion, the OT molecule rotates in the molecular plane around the center of mass during the electronic excitation from S_0 to S_1. The structural change is graphically represented in Figure 6. The rotation of OT taking place during the electronic excitation is nearly the same motion as the v_{51} mode. Therefore, the v_{51} mode is excited in the $S_1 \leftrightarrow S_0$ transition and therefore long progressions of the v_{51} mode should appear in the FE spectrum as observed in this work.
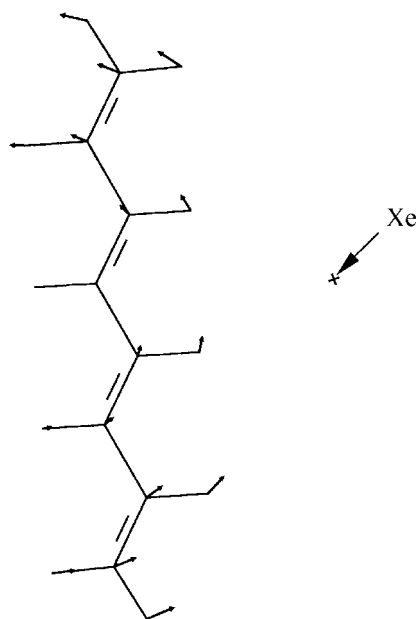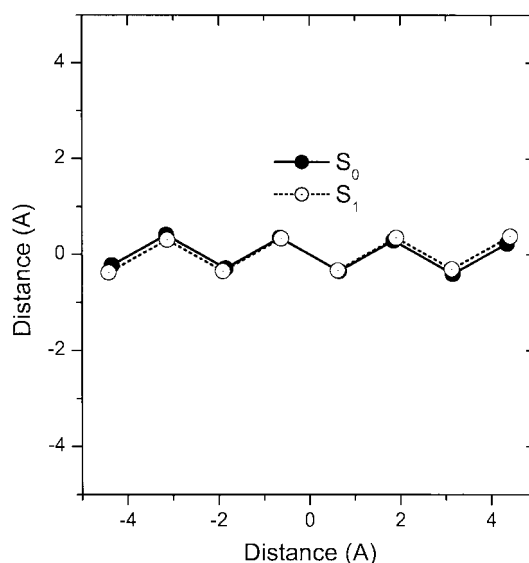

Figure 5. Vectorial representation of the lowest frequency mode (v_{51}) of OT-Xe. The vibrational motion is mainly the rocking of the OT moiety with respect to the Xe atom.

Figure 6. Change of the structures of octatetraene upon the $S_1 \leftarrow S_0$ ($2^1A_g \leftarrow 1^1A_g$) electronic excitation. The two central C-C bonds are overlapped to show the structural change. For simplicity, only the carbon atoms are drawn. The well-known bond-order inversion rotates the whole molecule during excitation.

Table 2 shows that the larger clusters have higher frequencies than the smaller ones. It can be understood from the fact that an additional Xe atom will exert an attraction or repulsion to the existing Xe atom depending upon the relative positions, which makes the potential along the short axis narrower. The narrower potential will give the higher values of the force constant and vibrational frequencies, as observed in this work.

In this paper, mostly qualitative interpretations are provided for the experimental observations in the FE spectrum and the fluorescence lifetimes. More quantitative understanding requires higher-level quantum mechanical calculations that give more accurate interaction potentials, vibrational frequencies, and the most stable structures for the OT-Xe$_n$ van der Waals clusters.

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