# The Two-Photon Excitation Spectrum of Phenanthrene Crystal

Hiroshi Otokozawa, Shigehiro Inomata, Naohiko Mikami, and Mitsuo Ito
*Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba, Sendai 980*
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The two-photon excitation spectrum of phenanthrene crystal was measured and compared with the corresponding usual one-photon absorption spectrum. It was found that the two-photon spectrum consists of a one-photon like system and a system characteristic of a two-photon process. The vibronic couplings in phenanthrene were discussed on the basis of the observed results.

The two photon excitation spectra of benzene and naphthalene have recently been studied by many workers.[1-9] The most characteristic feature of the two-photon absorption of these molecules from the ground state to the lowest excited electronic state $^1B_{2u}(L_b)$ is the appearance of strong vibronic bands involving a $b_{2u}$ vibration whose frequency in the excited state is about 1500 $cm^{-1}$. This is regarded as evidence of vibronic coupling involving the ground state.[10]

For both phenanthrene and naphthalene, the lowest excited electronic state is $^1L_b$. For phenanthrene, it is $^1A_1(L_b)$, for which both one-photon and two-photon transitions from the ground state are allowed under the molecular symmetry $C_{2v}$. (See Fig. 1.) This is in contrast to naphthalene, where the transition to the $^1B_{2u}(L_b)$ state is one-photon allowed but two-photon forbidden. The purpose of the present work is to see how different the one-photon and two-photon spectra are for phenanthrene, where the electronic transition is simultaneously allowed by both one-photon and two-photon selection rules.

Phenanthrene was purified by zone refining. The single crystal was grown by the Bridgman method, and the ab cleavage plane was normal to incident light. The two-photon excitation spectra were measured at 4.2 K by irradiating with a dye laser over the tunable wavelength region between 580 and 700 nm and detecting the resulting fluorescence. These two-photon energies cover the entire spectral region of the lowest excited electronic state of phenanthrene (300 to 350 nm). The method of the spectral measurements is the same as that reported in our previous paper.[9] The accuracy of the observed frequencies is ±2 $cm^{-1}$ for sharp bands. It was found that a trace of anthracene remaining in the phenanthrene crystal as an imputiry serves as an efficient fluorescence sensitizer. Polarization measurements were attempted. However, no significant difference was found between the main bands of the spectra with light polarized parallel to either the a or the b axis of the crystal. The two-photon excitation spectrum was observed also for the mixed crystal of biphenyl at 4.2 K. It was found that the spectrum of the mixed crystal is essentially the same as that of the pure crystal.

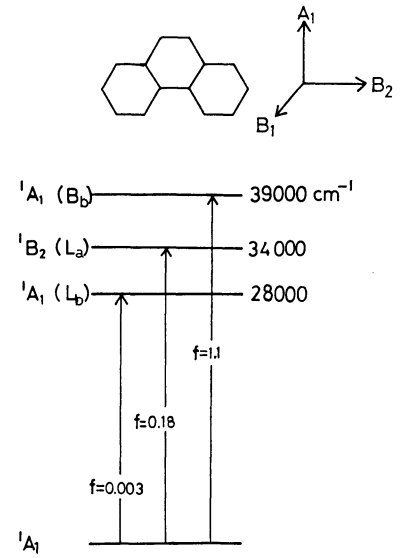


Fig. 1. Low lying electronic states of phenanthrene.

Figure 2 shows the two-photon excitation spectrum of the phenanthrene crystal, together with the corresponding usual absorption spectrum reproduced from a paper by Craig and Gordon.[11] Table 1 lists the observed frequencies of the main bands. It is seen from Fig. 2 that the 0,0 band appears strongly in the two-photon spectrum. This indicates that the electronic transition $^1A_1(L_b)$—$^1A_1$ is two-photon allowed as expected. Details of the Davydov splitting of the 0,0 band are somewhat different for the one-photon and the two-photon cases. In both spectra the lower frequency Davydov component is very sharp and has the same frequency. On the other hand the higher frequency component is very broad in the two-photon spectrum but is sharp in the one-photon spectrum. The maximum of the higher frequency component is

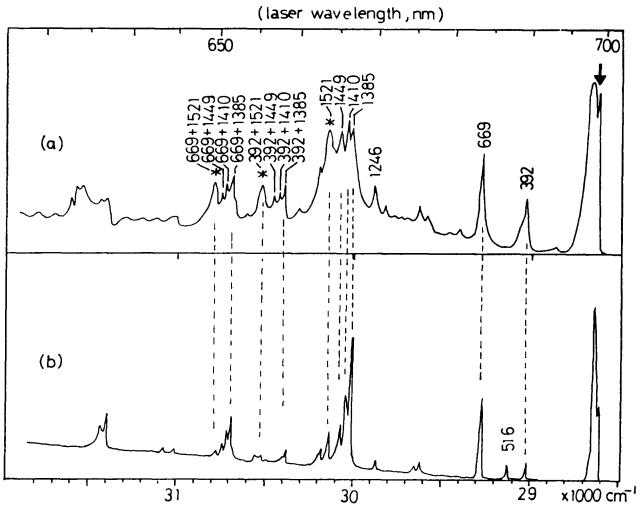


Fig. 2. (a) Two-photon excitation spectrum of phenanthrene crystal at 4.2 K. (b) One-photon absorption spectrum of phenanthrene crystal at 4.2 K taken from Ref. 11. The arrow indicates the position of the average frequency of the Davydov components of the one-photon 0,0 band (28627 $cm^{-1}$).

Table 1. One-photon and two-photon absorptions of phenanthrene crystal at 4.2 K

| One-photon (Craig, Gordon[11]) | | | Two-photon (present work) | | | Analysis |
|---|---|---|---|---|---|---|
| $\nu$ ($cm^{-1}$) | $\nu$ ($cm^{-1}$) | Rel. int. | $\nu$ ($cm^{-1}$) | $\nu$ ($cm^{-1}$) | Rel. int. | |
| 28597 Av. 28656 28627 | 0 | vs vs | 28599 (one photon: 28663 28627) | 0 | vs, sh vs, br | 0 |
| 29022 | 395 | m | 29019 | 392 | m | 392 $a_1$ |
| 29143 | 516 | m | | | | 516 $a_1$ |
| 29298 | 671 | s | 29296 | 669 | s | 669 $a_1$ |
| | | | 29582 | 955 | w | 955 $a_1$ |
| 29632 | 1005 | w | 29630 | 1003 | w | 1003 $a_1$ |
| 29881 | 1254 | w | 29873 | 1246 | m | 1246 $a_1$ |
| 30003 | 1376 | vs | 30012 | 1385 | s | 1385 $a_1$ |
| 30034 | 1407 | vs | 30037 | 1410 | s | 1410 $a_1$ |
| 30073 | 1446 | s | 30076 | 1449 | s | 1449 $a_1$ |
| 30146 | 1519 | m | 30148 | 1521 | s, br | 1521 $a_1$ |
| 30215 | 1588 | m | 30209 | 1582 | w | 1582 $a_1$ |
| | | | 30313 | 1686 | w | 669+1003 |
| 30405 | 1778 | w | 30405 | 1778 | m | 392+1385 |
| | | | 30449 | 1822 | w | 392+1410 |
| | | | 30481 | 1854 | w | 392+1449 |
| 30525 | 1898 | w | | | | 516+1385 |
| 30555 | 1928 | w | 30549 | 1922 | m, br | 392+1521 |
| | | | | | | 516+1416 |
| 30680 | 2053 | s | 30684 | 2066 | m, sh | 669+1385 |
| 30708 | 2081 | m | 30717 | 2090 | m, sh | 669+1410 |
| 30747 | 2120 | w | 30760 | 2133 | w | 669+1449 |
| 30821 | 2194 | w | 30817 | 2190 | m, br | 669+1521 |
| 31378 | 2751 | s | 31392 | 2765 | m, br | 2×1385 |

also shifted by 7 $cm^{-1}$ toward higher frequency from the corresponding one-photon peak. The breadth and frequency shift of the higher frequency band suggest a considerable contribution by a low frequency lattice phonon to the intensity of the 0,0 band of the two-photon spectrum. Coupling with the phonon is also suggested for other broad vibronic bands.

In our vibrational analysis of the two-photon excitation spectrum, the average frequency of the Davydov components of the one-photon 0,0 band (28627 $cm^{-1}$)[11] was taken as the origin from which frequency differences of the main vibronic bands were measured. It is seen from Fig. 2 and Table 1 that the observed frequency differences of the main bands agree very well with those of the one-photon spectrum within experimental error. There is a one-to-one correspondence between the one-photon and two-photon spectra for all the main vibronic bands, showing again the simultaneous one-photon and two-photon allowed transition.* However, the relative intensities of the vibronic bands are somewhat different in the two spectra. The two-photon vibronic bands can be classified into two groups, **A** and **B**, on the basis of their relative intensities in comparison with the intensities of the corresponding one-photon bands. The bands belonging to groups **A** are those for which the intensities relative to that of the 0,0 band are similar to those of the one-photon spectrum. The main bands in this group are 392, 669, 1385, 1410, 1449 $cm^{-1}$ and their combinations. With a few exceptions they are generally very sharp. Group **B** consists of the vibronic bands involving 1521 $cm^{-1}$ shown by asterisk in Fig. 2. These bands are weak in the one-photon spectrum, but fairly strong in the two-photon spectrum. They are also characterized by their broadness.

According to the ordinary absorption studies of the pure and mixed crystals of phenanthrene by Craig and Gordon[11] and by Hochstrasser and Small,[12] all the main bands in the **A** system involve totally symmetric vibrations in the excited state. The most interesting feature of the **A** system is the origin of the 669 $cm^{-1}$ band. Craig and Gordon,[11] Hochstrasser and Small,[12] and Craig and Small[13] concluded that the 669 $cm^{-1}$ band in the one-photon spectrum borrows part of its intensity from higher excited electronic states by vibronic coupling. Since 669 $cm^{-1}$ is a totally symmetric vibration, this is an interesting example of vibronic coupling through a totally symmetric vibration. If this interpretation is correct, we expect some difference in the intensity of the 669 $cm^{-1}$ band relative to that of the 0,0 band between the one-photon and two-photon spectra, because vibronic coupling schemes reflected in the two spectra are generally different. On the other hand, if the 0,1 band is not a vibrationally induced one, the relative intensity should be equal both for the one-photon and the two-photon spectra.

It is difficult to compare quantitatively the intensity

* The one-photon band, 0,0+516 $cm^{-1}$ is missing in the two-photon spectrum. This will be discussed later.

ratio of the 0,0 band and the 0,0+669 $cm^{-1}$ band in the two spectra because of rather large errors in the intensity estimation. However, qualitatively the observed ratios are not greatly different. At least the intensity relation between the 0,0 band and the 0,0+669 $cm^{-1}$ band is similar in the two spectra. The intensity of the 669 $cm^{-1}$ band relative to the 1385 $cm^{-1}$ band, which has a non-vibronic origin according to Craig and Small[13], is also similar. These facts seem to support a non-vibronic origin for the 669 $cm^{-1}$ band, contrary to the conclusion of Craig *et al.* However our qualitative intensity data are not good enough to derive a definite conclusion at the present time. We merely point out here that comparison between the relative intensities of one-photon and two-photon spectra may provide an additional clue for the origin of vibronic bands.

We shall consider next the **B** system, which consists of the vibronic bands involving the totally symmetric excited-state frequency of 1521 $cm^{-1}$. The **B** system is fairly strong in the two-photon spectrum and weak in the one-photon one. As mentioned before, the strong appearance of vibronic bands whose excited-state frequency is about 1500 $cm^{-1}$ is a common characteristic of the $^1L_b$—$^1A$ two-photon absorption spectra of benzene and naphthalene.[1-9] Therefore, the **B** system of phenanthrene may be assumed to arise from the same cause as that of benzene and naphthalene. The effective vibrations of benzene and naphthalene are bond alternating C–C stretching modes. In benzene they are $\nu_{14}(b_{2u})$ (1566 $cm^{-1}$ in the $^1B_{2u}(L_b)$ state and 1309 $cm^{-1}$ in the ground state) and in naphthalene $\nu_{21}(b_{2u})$ (1535 $cm^{-1}$ in $^1B_{2u}(L_b)$ state and 1361 $cm^{-1}$ in the ground state). Mikami and Ito[10] concluded that these vibronic bands are due to vibronic coupling between the ground state and the lowest excited $^1B_{2u}(L_b)$ state through these vibrations. The excited-state vibration at 1521 $cm^{-1}$ of phenanthrene probably corresponds to $\nu_{14}$ of benzene and $\nu_{21}$ of naphthalene, although it is a totally symmetric vibration in phenanthrene because of reduction of the molecular symmetry. Assuming that the vibronic coupling involving the ground state is similar to the cases of benzene and naphthalene, the corresponding ground state frequency should be smaller than 1521 $cm^{-1}$. It is expected to be between 1300 and 1400 $cm^{-1}$ by analogy to benzene and naphthalene. There are several totally symmetric vibrations in this frequency region.[14] Unfortunately, it is difficult to pick a specific one because of the lack of knowledge about the detailed vibrational modes.

Finally, it may be worthwhile to mention that the moderately intense one-photon vibronic band 0,0+516 $cm^{-1}$, reported by Craig and Gordon[11] is entirely missing in our two-photon spectrum (see Fig. 2). In the one-photon spectrum it has about the same intensity as that of the nearby band 0,0+392 $cm^{-1}$. The latter appears with a considerably intensity in the two-photon spectrum, but the former is absent. This suggests that the 0,0+516 $cm^{-1}$ band has a vibrationally induced origin which occurs selectively in the one-photon spectrum. The excited-state vibration of 516 $cm^{-1}$ was assigned by Craig and Gordon[11] and by Hochstrasser and Small[12] to a totally symmetric vibration. The frequency is close to the excited-state $\nu_6(e_{2g})$ mode of benzene at 520 $cm^{-1}$ [15] (606 $cm^{-1}$ in the ground state) and to the excited-state $\nu_{33}(b_{3g})$ of 438 $cm^{-1}$ of naphthalene[16] (506 $cm^{-1}$ in the ground state). These vibrations are well known to be the most effective perturbing vibrations in mixing the $^1L_b$ states and $^1B$ states of benzene and naphthalene. Therefore, it is highly probable that the totally symmetric 516 $cm^{-1}$ vibration of phenanthrene is the perturbing vibration coupling the lowest excited $^1A_1(L_b)$ state and the third lowest $^1A_1(B_b)$ state of this molecule.

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