The Resonance Raman Effect of Azobenzene and *p*-Aminoazobenzene

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The resonance Raman spectra of azobenzene and *p*-aminoazobenzene were measured precisely at various excitation wavelengths. It was found that the π–π^* excited state played a dominant role in the Raman intensities but not the n–π^* excited state and that there was no correlation between the Raman intensity and the absorption coefficient at excitation wavelength.

Resonance Raman effect (RRE) is observed[1,2] when the frequency of Raman exciting light falls in the electronic absorption. One of the characteristic aspects of RRE is enormous enhancement of Raman intensity. In general, aromatic molecule has more than two absorptions in the visible and ultra-violet regions. Thus, it is interesting to see what difference occurs in the intensity enhancement when the excitations are made at different wavelengths which coincide with the absorptions of different electronic transitions of the molecule.

Azobenzene is suitable for such an experiment. It has two different electronic absorption bands centered at 450 and 320 nm (Fig. 1), which are assigned to n-π^* and π–π^* transitions, respectively[3,4]. Moreover, two different lasers whose lasing wavelengths fall in the above absorptions are now available.

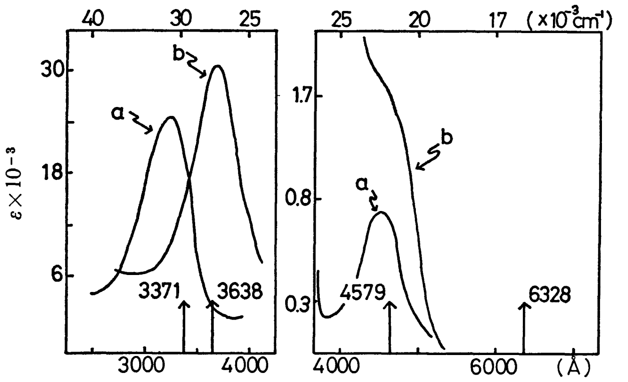

Fig. 1. The electronic absorption spectra of azobenzene and *p*-aminoazobenzene in the visible and ultraviolet regions.
a: Azobenzene in carbon tetrachloride.
b: *p*-Aminoazobenzene in carbon tetrachloride.

The Raman spectra of azobenzene and its derivatives excited by visible Hg lines have been reported by Brandmuller and Hacker,[5] who observed the intensity enchancement of several Raman lines in resonant condition with the n-π^* excited state.

We have studied the wavelength dependence of the Raman intensities of azobenzene and *p*-aminoazobenzene with various kinds of lasers covering from visible to near ultraviolet regions. It was concluded from the results that the excited electronic states corresponding to π–π^* absorptions were primarily important in RRE.

Experimental

Experimental details for taking Raman spectra have been described.[6] The exciting light sources used were a 6328 Å He–Ne laser, a 4579 Å Ar ion laser and a 3371 Å nitrogen pulsed laser. The 3638 Å lasing line of the Ar ion laser was also used.

The sample solution was prepared by dissolving the stock solution of benzene containing known amounts of the sample in an appropriate solvent (carbon tetrachloride or chloroform). Depending on the excitation wavelengths used, the concentration of the solution was so adjusted as to obtain the maximum efficiency. The concentrations appropriate to 6328, 4579, 3638 and 3371 Å excitations are about 10^{-1}, 10^{-4}, 10^{-4} and 10^{-5} mol/*l*, respectively. The intensities of the Raman lines of the sample were determined relative to the 992 cm^{-1} Raman line of benzene which was used as an internal standard for intensity.

The observed intensities of the individual Raman lines should be corrected for absorption of the sample to obtain the original intensities. The correction was made by $I=I_{obs}\times 10^{\varepsilon c x}$, where I is the original Raman intensity, I_{obs} is the intensity observed after passing the sample solution of concentration c and path length x, and ε is the absorption coefficient at the wavelength of the Raman line concerned. x represents the distance between the incident laser beam and the wall of the sample cell through which the Raman scattering is observed. Since c and x were determined from the experimental conditions and ε was also known by the electronic absorption measurement, the original intensity I was determined from I_{obs}. Corrections for the wavelength dependence of the detection system as well as for polarization character of the monochromator were also carried out.

Results and Discussion

The intensities of several main Raman lines of the sample relative to the intensity of the 992 cm^{-1} line of benzene were evaluated from the integrated areas of the individual Raman line of the recorded spectral chart and the corrections described above were made to the observed intensities. The corrected relative intensities normalized for the intensities at 6328 Å excitation are given in Table 1 for various excitation wavelengths. Errors in the values are also listed. The

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TABLE 1. THE WAVELENGTH DEPENDENCES OF RAMAN INTENSITIES[a]

Excitation wavelength		6328Å	4579Å	3638Å	3371Å
Azobenzene	1140 cm^{-1}	1	4	30	60
	1182 cm^{-1}	1	6	—[b]	80
	1440 cm^{-1}	1	4	60	90
p-Amino-azobenzene	1139 cm^{-1}	1	10	100	100
	1184 cm^{-1}	1	9	—[b]	200
	1422 cm^{-1}	1	20	200	300

a) The corrected relative Raman intensities of azobenzene and *p*-aminoazobenzene are normalized for the intensities at 6328Å excitation. Experimental errors at 4579 Å, 3638Å and 3371Å are ±20%, ±30% and ±30%, respectively.

b) The Raman line around 1180 cm^{-1} at 3638Å excitation is far weaker than the other Raman lines, so that it is not possible to obtain the quantitative value.

errors are due to the low signal to noise ratio and the relatively small magnitude of the signals. In spite of the large errors, the following discussions are possible through repeated measurements. The Raman line of 1440 cm^{-1} of azobenzene as well as the 1422 cm^{-1} line of *p*-aminoazobenzene has been assigned as due mainly to the N=N stretching vibration.[7–9] The vibrational modes of the other Raman lines around 1140 and 1180 cm^{-1} are not well established.

As seen in Table 1, the N=N stretching vibration undergoes more or less stronger enhancement than the other two Raman lines under rigorous resonant conditions (3638 and 3371 Å excitation). This indicates the close connection between the nature of the enhanced vibration and the electronic absorption band (the intramolecular charge transfer from benzene to the N=N group). It is concluded from the measurements at the two excitation wavelengths (3638 and 3371 Å) falling in the same π-π^* transition band that there is no correlation between the enhanced degree of the Raman line and the absorption coefficient at the excitation wavelength. This is clearly seen in the case of azobenzene. The degrees of enhancement differ at most twice in spite of the enormous distinction of the absorption coefficients at the two wavelengths (the molar absorption coefficients are 4.6×10^2 at 3638 Å and 2.0×10^4 at 3371 Å, respectively).

Mortensen[10] reported that the enhanced degree of Raman line was proportional to the square of the absorption coefficient at the excitation wavelength. Kiefer and Bernstein[11] asserted linear proportionality between these two quantities. Our result does not fit with either of these and further consideration is required.

For the RRE in the n-π^* absorption region by 4579 Å excitation, the relative intensities at the 4579 Å excitation (Table 1) do not seem to be as large as expected from the rigorous resonant condition. They seem to be of an order of magnitude anticipated from the preresonance effect contributed from the higher excited state. In order to see this, the wavelength dependences of the relative intensities of the Raman lines of azobenzene were calculated by means of the equation given by Albrecht and Hutley.[12] Assuming only the π-π^* excited state of azobenzene corresponding to the 320 nm absorption to be responsible to the preresonance effect, the relative intensities[13] at 4579 Å excitation were calculated to be about four times the intensity at 6328 Å, in which the wavelength dependence of the reference Raman line of benzene was taken into account by postulating the excited state corresponding to the 180 nm band of benzene as an active intermediate state.[12] The calculated value is of about the same order of magnitude as the observed values given in Table 1. The fairly large observed intensities at 4579 Å excitation for *p*-aminoazobenzene can also be explained by the closer preresonant condition achieved by the shift of the π-π^* absorption toward longer wavelength (the maximum peak of the π-π^* absorption of *p*-aminoazobenzene is located at 370 nm).

Thus it may be concluded qualitatively that the π-π^* excited states of azobenzene and *p*-aminoazobenzene play a dominant role in the Raman intensities but not n-π^* excited state.

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[13] In this case, we considered to totally symmetric vibrational modes and $F_A{}^2$ term. (See Eq. (5′) in Ref. 12)