

Adsorption of 2-Cyanonaphthalene on Silver Sol Investigated by Raman Spectroscopy[†]

Sung Hyun Park, Eunah Lee, Du-Jeon Jang*, Myung Soo Kim*, and Kwan Kim*

Department of Chemistry, College of Natural Sciences, Seoul National University Seoul 151-742, Korea

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Surface-enhanced Raman (SER) scattering of 2-cyanonaphthalene (2-CN) has been investigated in silver sol. Addition of halide ions was needed to obtain authentic SER spectra of the molecule. The SER spectra thus obtained exhibited a slight but noticeable dependence on the kind of halide ions used. This halide-dependent spectral variation was attributed to the orientational change of molecule on silver sol surface. A possible mechanism for such an orientational change is proposed in terms of the competitive adsorption of 2-CN with halide ions on the so-called halide-specific sites.

Introduction

Surface-enhanced Raman scattering (SERS)¹⁻⁴ has been established as a useful technique for the spectroscopic investigation of surface adsorbates. The identity of the chemical species adsorbed and their conversion *via* surface reactions can be probed using this technique.⁵⁻⁸ In addition, analysis of spectral features such as relative intensities of vibrational bands and their shift and broadening upon surface adsorption provides valuable information on the adsorption mechanism.⁹⁻¹¹

To get the SER spectra in silver sol, aggregation of the silver sol particles is prerequisite. Most of the nitrile compounds investigated so far were ineffective in inducing the aggregation. Hence, various inorganic reagents, *e.g.* Ba(NO₃)₂, NaBH₄, BaX₂ (X=Cl, Br, I), etc., were added together with nitrile compounds to induce the aggregation.¹²⁻¹⁴ 2-Cyanonaphthalene (2-CN), which is the target molecule of the present investigation, was also ineffective to induce the aggregation. Most of the aggregating reagents except for BaX₂ were inappropriate to record the SER spectra of 2-CN because the resulting solution did not show large surface enhancement or produced Raman spectra that can not be correlated with the ordinary Raman (OR) spectrum of 2-CN.

As implied in the above description, halide ions (Cl⁻, Br⁻, I⁻) were found, nonetheless, useful to produce SER spectra of high quality. However, the SER spectra thus obtained exhibited a slight but noticeable dependence on each halide used. As a continuation of our effort to understand the influence of the halide coadsorption on the SER spectra and the nature of the surface sites on the sol particle, details of the SER spectral variation of 2-CN have been investigated.

Experimental

The method of preparation of aqueous silver sol has been reported previously.¹⁵ A methanolic solution of 5×10⁻² M 2-CN was added to silver sol, and Cl⁻, Br⁻, or I⁻ was added subsequently to induce the aggregation of the silver sol par-

ticles. The final concentration of 2-CN in silver sol solution was 4.7×10⁻⁴ M. After the color of sol solution changed from yellow to green or blue, polyvinylpyrrolidone (PVP, MW 40000) was added as a colloid stabilizer. Stock solutions of 3×10⁻² and 3×10⁻⁴ M BaX₂ (X=Cl, Br, I) were used to examine the concentration effect of halides.

A Japan Spectroscopic Model R-300 Raman spectrometer operated with 514.5 nm radiation from an argon ion laser (Spectra-Physics Model 164-06) was employed to obtain the Raman spectra. Glass capillaries were used as sampling devices. Raman scattering was observed at 90° geometry using a photon counting system interfaced with a personal computer. In a typical experiment, the laser power was 80-100 mW at the sample position and the spectral slit width was 5-10 cm⁻¹. All chemicals were of reagent grade and triply distilled water was used throughout.

Results and Discussion

As was described in Introduction, halides were effective in inducing the aggregation of sol particles and generating SER spectra of 2-CN that can be correlated with the ordinary Raman (OR) spectrum. Chloride ion was the most efficient agent and the iodide ion was, on the other hand, the least efficient.

Figure 1(a) shows the OR spectrum of neat 2-CN in solid state. Its spectral assignments listed in Table 1 are made by correlating the observed peaks to those of naphthalene and halonaphthalene molecules.^{16,17} Figure 1(b), 1(c), and 1(d) represent the SER spectra of 2-CN obtained in the presence of Cl⁻, Br⁻, and I⁻ ions, respectively. Although the absolute enhancement was affected to some degree, the SER spectral pattern was hardly dependent on the extent of colloidal aggregation. As can be seen in Figure 1, the relative peak intensities in the three SER spectra were, however, clearly different from one another. Nonetheless, the peak positions were, in contrast, similar to one another, as can be seen in Table 1. Moreover, the peaks in the SER spectra could be correlated well with those in the OR spectrum. For example, the major ring modes at 507, 763, 1017, 1121, 1158, 1379, 1431, 1463, and 1623 cm⁻¹ in the OR spectrum have their counterparts at 508, 766, 1017, 1120, 1160, 1382, 1434, 1462, and 1621 cm⁻¹ in the SER spectrum taken in the presence

[†]Dedicated to Prof. Woon-Sun Ahn on the occasion of his retirement.

*To whom all correspondence should be addressed.

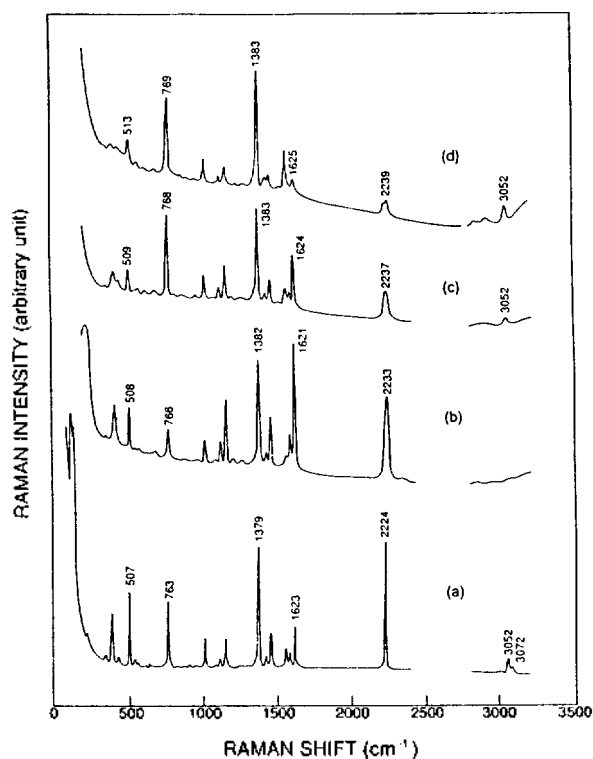


Figure 1. (a) OR spectrum of 2-cyanonaphthalene (2-CN) in solid state. SER spectra of 2-CN in silver sol with 2.2×10^{-3} M of (b) Cl^- , (c) Br^- , and (d) I^- .

of Cl^- . This means that the species responsible for all the SER spectra shown in Figure 1 is 2-CN.

When a molecule chemisorbs on the surface, frequencies of some of its vibrational modes, especially those involving the atom(s) participating in the adsorption, change from the corresponding values in the unadsorbed state. Since the changes in the peak position and the bandwidth of ring modes are not noticeable in the SER spectra of 2-CN, the surface-ring π orbital interaction seems insignificant. On the other hand, a substantial spectral change was observed for the CN stretching ($\nu(\text{CN})$) vibration. Upon surface adsorption, the $\nu(\text{CN})$ band blue-shifted by $9\text{--}15\text{ cm}^{-1}$ along with $22\text{--}33\text{ cm}^{-1}$ increase in its bandwidth. Namely, the band appeared at 2224 cm^{-1} with 14 cm^{-1} bandwidth in the OR spectrum, but at 2233 , 2237 , and 2239 cm^{-1} with 47 , 47 , and 36 cm^{-1} bandwidths in the SER spectra taken in the presence of chloride, bromide, and iodide, respectively. This observation implies that 2-CN is adsorbed on the silver surface *via* its nitrile group.

In organometallic chemistry of nitrile derivatives,^{18–21} the linear coordination to a metal atom through the nitrogen lone pair electrons is known to increase the CN stretching frequency from that in free state. On the other hand, coordination through the CN π system results in a decrease of the frequency. Referring to the blue-shifts observed for 2-CN, this organometallic spectral correlation scheme dictates the molecule to be adsorbed on silver *via* the nitrogen lone pair electrons. In such a bonding, the molecular plane will take a perpendicular orientation with respect to the surface plane rather than a flat one. Such a picture looks to be in

Table 1. Spectral data and vibrational assignments for 2-cyanonaphthalene

ORS (solid)	Wavenumber/ cm^{-1}			Vibrational Assignment ^c
	SERS with Cl^-	SERS with Br^-	SERS with I^-	
	221			ν (Ag-Cl)
348	352	353		α (CCC) b_{2u}
392		387	390	α (CCC) a_u
	410	412		ϕ (CC) b_{2g} b
432		453	434	β (CX) b_{2u} c
507	508	508	513	ϕ (CC) b_{1g}
560		564	564	α (CCC) a_g
613		618		ϕ (CC) a_u b
763	766	768	769	ν (CC) a_g
1017	1017	1016	1016	ν (CC) a_g
1121	1120	1120	1118	β (CH) b_{3u} b
1158	1160	1159	1159	β (CH) a_g
1379	1382	1383	1383	ν (CC) a_g
1431	1434	1430	1430	ν (CC) b_{1g} b
1463	1462	1462	1459	ν (CC) b_{1u} c
1568	1569	1567	1568	ν (CC) a_g
1592	1592	1593		ν (CC) b_{2u} b
1623	1621	1624	1625	ν (CC) b_{1g} b
2224	2233	2237	2239	ν (CN) b
3052		3052	3052	ν (CH) c
3072				

^aRef. 16 and 17. (ν : stretching, α : angle deformation, ϕ : non-planar torsion, β : in-plane bending). ^bRelatively more enhanced with Cl^- . ^cRelatively more enhanced with Br^- or I^- .

conformity with the previous argument that the possibility of direct surface-ring π orbital interaction is scarce. However, as will be discussed below, this adsorption mechanism is in apparent contradiction to the surface orientation of 2-CN assumed specifically when Cl^- is co-present in silver sol.

Based on the organometallic spectral correlation scheme, the subtle spectral difference among the SER spectra shown in Figure 1 may be simply attributed to difference in the adsorbate orientation. In this regard, it would have been useful if a clear-cut surface selection rule had been established for SERS. At the moment, it is known that the surface selection rule derived from the electromagnetic enhancement theory^{22,23} is applicable only to limited types of normal modes. In particular, the C-H symmetric stretching ($\nu(\text{CH})$) vibrations of aromatic rings are known to be unambiguous probes for determination of adsorbate orientation. Namely, the corresponding band is relatively more enhanced when the ring plane assumes perpendicular stance to the surface plane than when it lies parallel to the surface. The $\nu(\text{CH})$ band of 2-CN appeared, in fact, distinctly at 3052 cm^{-1} in the SER spectra taken in the presence of iodide and bromide [see Figure 1(c) and 1(d)]. This supports the aforementioned bonding scheme of 2-CN on silver. It has to be noted, however, that $\nu(\text{CH})$ is hardly observable in the SER spectrum of 2-CN when chloride ions are coadsorbed on the sol particle surface [see Figure 1(b)]. This suggests that the planar ring portion of 2-CN lies down flat on the surface when chloride

ions are coadsorbed.

In a flat orientation, bonding will be more likely to occur through the CN π system rather than through the nitrogen lone pair electrons. This view is obviously in conflict with the organometallic spectral correlation scheme. A similar situation has been encountered in our recent SERS study on conjugated aromatic nitriles such as 1,4-dicyanobenzene, 4-cyanobenzoic acid, and 4-aminobenzonitrile.^{24,25} Namely, all of these molecules were found to adsorb on the silver surface *via* their two substituents at para positions with flat stances, suggesting the nitrile groups to interact with the surface *via* the π systems. As expected, $\nu(\text{CH})$ bands were absent in the SER spectra. However, the CN stretching vibrations blue-shifted upon surface adsorption. Analyzing the compiled SERS data, the blue-shift in the CN stretching vibrations upon adsorption could be attributed to disruption of conjugation rather than due to end-on coordination. Namely, a caution is needed in the application of the spectral correlation scheme found from the organometallic chemistry to the surface vibrational spectroscopy. Difference may arise from the fact that one often observes weakly chemisorbed species in the surface vibrational spectroscopy. Based on the above argument, 2-CN may be concluded to adsorb on the silver surface *via* the CN π system when chloride ions are co-present in the sol medium. One may argue, however, that a flat orientation will be accompanied also by the surface-ring π orbital interaction. We have already mentioned that such a direct interaction seems infeasible since the peak positions and the bandwidths of ring modes are comparable in the OR and SER spectra. This fact indicates that 2-CN assumes a slightly tilted stance with respect to the surface plane rather than a completely flat one in the presence of chloride ion. This model is supported further by the fact that the C-H stretching band is, although very weak, discernible in the SER spectrum taken with a red-sensitive detector even when chloride ions are co-present in the sol medium.

In addition to $\nu(\text{CH})$ and $\nu(\text{CN})$ bands, a conspicuous spectral variation with halide species is observed for the bands at around 765, 1160, 1460, and 1620 cm^{-1} . The first peak is stronger in the SER spectrum obtained in the presence of bromide or iodide, but the other three peaks are substantially weaker compared with the corresponding peaks observable in the presence of chloride. Even though such spectral variations are likely related to the difference in the surface orientation of 2-CN, details can not be understood in the absence of a reliable surface selection rule. Peaks displaying intensity change with halide species are marked in Table 1.

Several different mechanisms may be invoked to explain the halide-dependent orientational variation of 2-CN. Firstly, it may be possible that the orientational difference of the molecule originates simply from the difference in steric hindrance. Since the size of the iodide ion is 1.25 times larger than that of the chloride ion, the steric hindrance to the adsorption of 2-CN by iodide will be greater than by chloride. Accordingly, the perpendicular stance of 2-CN which suffers less steric hindrance than the parallel one may be favored with iodide. Situation is similar for bromide as well. In simple steric hindrance model, it is expected that the SER spectral feature with bromide would change to that with chloride at submonolayer coverage of bromide concentration. That

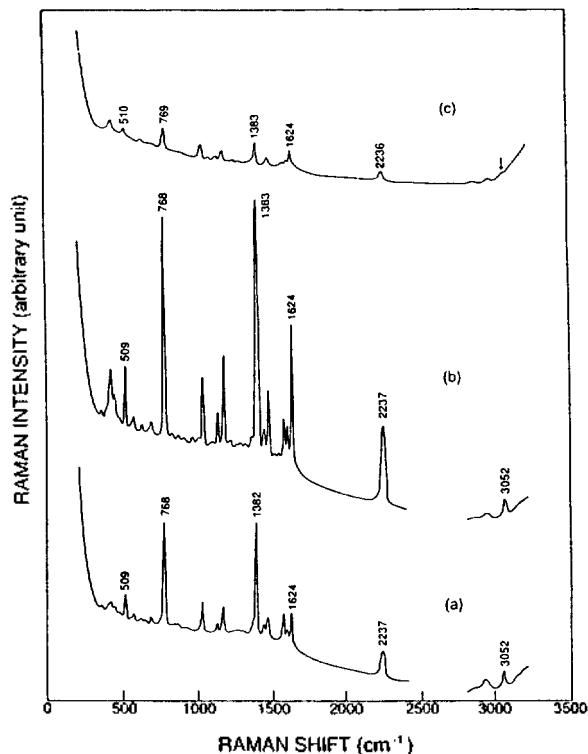


Figure 2. SER spectra of 2-CN in silver sol with Br^- concentration of (a) 1.1×10^{-3} M, (b) 1.1×10^{-4} M, and (c) 1.1×10^{-5} M.

is, when the coverage of bromide ion is below the monolayer limit, 2-CN may assume a flat orientation on the metal surface, resembling the case of chloride ion. Assuming that the average radius of the silver particle is 5 nm as reported previously^{15,26} and taking the radius of bromide ion as 1.96 Å, the bulk concentration of bromide ion needed for monolayer coverage is estimated to be 2.1×10^{-5} M. The SER spectra taken with bromide concentration well above and below this value do not display noticeable difference, as can be seen in Figure 2. In particular, the SER spectrum (Figure 2(c)) taken with submonolayer coverage of bromide does not become similar to the SER spectrum taken with chloride. Hence, the simple steric hindrance model does not seem to be appropriate to explain the spectral variation with halide species. For the case of iodide ion, it was not possible to obtain the SER spectrum at submonolayer coverage because the enhancement factor was too small.

The second possible mechanism for halide-dependent spectral variation is the formation of halide-mediated surface complexes in the form of 2-CN-X-Ag (X=Cl, Br, I). Depending on the kind of halide ion in the surface complex, the physico-chemical property of the complex would differ and accordingly exhibit different spectral pattern. To justify this argument, confirmation of the existence of such complex is needed. Attempt to synthesize such 2-CN-X-Ag complex was not successful. One can not rule out this model, however, because weakly bound complexes may be possible on the surface.

The third possible mechanism is based on the previous suggestions²⁷⁻²⁹ that halide ions on the silver surface could provide the SERS active sites. Each halide ion may form

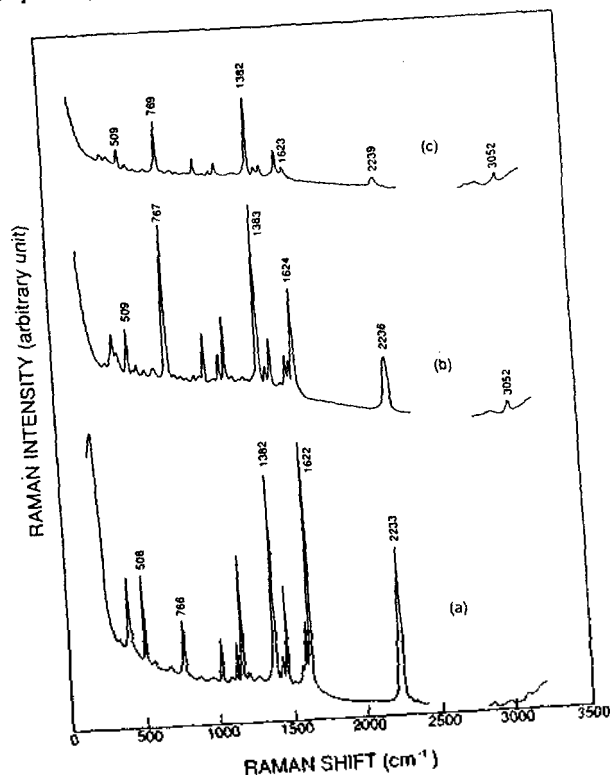


Figure 3. SER spectra of 2-CN in silver sol with Cl^- concentration of 1.1×10^{-3} M, in the presence of no other halides (a), and in the presence of additional halides with 1.1×10^{-3} M Br^- (b), and 1.1×10^{-3} M each of Br^- and I^- (c).

the active site with its own specific local structure, and the adsorption mechanism of 2-CN may be different depending on the microscopic local crystalline plane of the active sites. It is unfortunate that information on the microscopic local structure of the active site is not available at the moment even though the idea of different local structures for different halide ions seems to be somewhat farfetched.

So far, some mechanisms to explain the halide-dependent spectral variation have been considered, but none of them looks satisfactory. In order to characterize the SER spectral dependence on halide ions further, it has been attempted to compare the SER spectra of 2-CN obtained in the presence of halide mixtures at different concentrations. First of all, the SER spectra were obtained with either bromide or iodide ions added in excess (that is, far more than needed for full monolayer coverage) into the sol containing chloride ions, as shown in Figure 3. The spectral pattern for 2-CN changed concurrently from that obtainable in the presence of chloride to that in conformity with the added ions. This can be understood simply by invoking that the adsorption strength is in the order of $\text{I}^- > \text{Br}^- > \text{Cl}^-$.²⁷ On the other hand, when the amount of bromide or iodide ions added was varied from less to slightly higher than needed for monolayer coverage, the accompanying change in the spectral pattern appeared rather interesting. Namely, as is shown in the Figure 4, when bromide ions were added gradually into a sol containing chloride ions until the concentration of added bromide became higher than needed for the full surface coverage, the spectral pattern of 2-CN changed from that

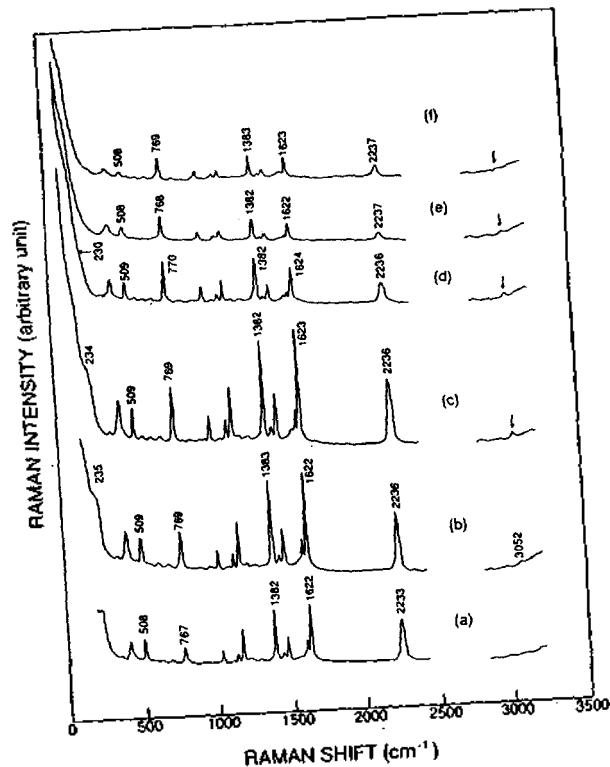


Figure 4. SER spectra of 2-CN in silver sol with Cl^- concentration of 1.1×10^{-4} M, in the presence of no other halides (a), and in the presence of additional Br^- with concentrations of (b) 2.9×10^{-6} M (1/8 coverage), (c) 5.8×10^{-6} M (1/4 coverage), (d) 1.1×10^{-5} M (1/2 coverage), (e) 2.2×10^{-5} M (full coverage), and (f) 4.3×10^{-5} M (more than needed for full coverage).

obtainable in the presence of chloride to that of bromide. This change was nearly complete when the amount of added bromide could cover one fourth of the silver sol surface. On the other hand, the Ag-Cl stretching band disappeared completely only at the full monolayer coverage of bromide ion. The following adsorption mechanism is proposed here which, we believe, can account for the above observation together with the halide-dependent spectral variation described previously.

It is likely that 2-CN adsorbs preferentially on the specific sites of the sol surface, competing with halide ions. It was suggested recently that the halide ions have a strong affinity for the so-called 'halide-specific sites' on the silver surface and that the fraction of these sites was estimated to be about one quarter of all the available sites on the silver sol surface.³⁰ Let us suppose that 2-CN also has an affinity to adsorb selectively on these halide-specific sites and competes with halide ions for surface adsorption. Let us further assume that the adsorption strength of the 2-CN on the sol surface is weaker than those of I^- and Br^- , but is stronger than Cl^- . Then, the following explanation is feasible for the observations made in Figure 4.

In the presence of chloride ions only (Figure 4(a)), 2-CN which is superior to chloride in surface adsorption can secure a surface site easily. Accepting the conclusion in a previous report²⁴ that the side-on coordination of the nitril group is energetically more favorable for aromatic nitriles

2-CN is likely to take a more or less flat stance on the surface in this case. When the submonolayer amount of bromide ions are added to the sol containing chloride ions (Figure 4(b) and (c)), bromide would compete with the adsorbed 2-CN for a surface site. Superior adsorption strength of bromide means that most of the adsorbed 2-CN will be replaced by Br^- and a small fraction will compete for the sites which are mostly occupied by Br^- . Limited surface area available for 2-CN would favor a perpendicular stance of the molecule. Even when the halide-specific sites are nearly completely occupied by Br^- , Ag-Cl stretching band may still appear in the SER spectrum due to the chloride ions adsorbed on the 'halide-non-specific sites'. When more bromide ions are added (Figure 4(d)), bromide ions begin to adsorb on the halide-non-specific sites replacing the adsorbed chloride ions. As the amount of bromide ions increases enough to cover the whole surface (that is, a monolayer coverage as shown in Figure 4(e) and (f)), all the adsorbed chloride ions are replaced by bromide ions eventually, and Ag-Cl stretching band appears no longer in the SER spectra. This picture is entirely consistent with the previous conclusion on the adsorption of halides on the silver surface. In conclusion, the present mechanism can be regarded as a competitive adsorption of 2-CN on the so-called halide-specific sites. Namely, the halide-dependent spectral variation which is attributed to the orientational change may arise from the steric hindrance functioning only at the limited area of the sol surface which is generally called halide-specific sites.

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