THE INFLUENCE OF A RESONATOR ON THE INTENSITY DISTRIBUTION IN RAMAN LIGHT-SCATTERING SPECTRA

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THE INFLUENCE OF A RESONATOR ON THE INTENSITY DISTRIBUTION IN RAMAN LIGHT-SCATTERING SPECTRA

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In the practice of molecular spectral analysis, a very important problem is increasing the brightness of the observed Raman scattering (r.s.) lines of light. The desired result has usually been obtained by improving the source of the exciting light. In this way an enhancement of the luminescence intensity by several times has been achieved (^{1}, ^{2}). A fundamentally new method for increasing the observed intensity of scattered light was proposed in (^{3}). The calculations carried out in that work show that, if the luminous object is placed in a Fabry–Perot interferometer, a considerable enhancement of the luminescence should be expected. Numerical calculations according to (^{3}) for a standard interferometer give an amplification on the order of 20. In connection with this, we carried out an experimental verification of the indicated result of the theoretical calculations.

The scheme of the setup we used is shown in Fig. 1. The cell Q was made in such a way that its outer side faces were parallel to one another with an accuracy of up to $5''$. The alignment of the entire setup was performed with an AKT-400 autocollimator with an accuracy of up to $1''$. Mirrors from a standard ITsS-9 interferometer were used in the resonator. The r.s. spectra were recorded with the aid of a DFS-4 spectrometer modernized by us (^{4}). The accuracy of the measurements of the integral intensity was 5%.

The measurement results showed that, indeed, when r.s. is excited in a Fabry–Perot interferometer, the intensity of the scattered light increases by an order of magnitude. However, because of absorption and reflection at the front mirror (transmission coefficient 0.112), the intensity of the scattered light emerging from the resonator remained practically unchanged. Thus, the method for increasing the r.s. intensity, in the form in which it was proposed in (^{3}), proved ineffective.

In the course of further experimental investigation, we discovered an extremely interesting resonator effect: the distribution of energy in the r.s. spectrum obtained by the usual method with the use of a Vud cell differs substantially from

Fig. 1. Diagram of the setup.

Figure 1: Fig. 1. Diagram of the setup.

the distribution of energy in the r.s. spectrum obtained with an interferometer. The measurement results are presented in Table 1.

In all cases, in the resonator there was observed a relative increase in the r.s. spectra of depolarized lines ($\rho \sim 0.8$) in comparison with polarized ones ($\rho < 0.2$). Thus, for example, in the case of benzene, the intensity of the line $\nu = 1178$ cm^{-1} ($\rho = 0.86$) in comparison with the line $\nu = 992$ cm^{-1} ($\rho = 0.1$) increased by a factor of 2 as a consequence of the resonator effect; an analogous relative increase is also observed for some lines of toluene.

The experimental fact we have discovered cannot be explained by trivial polarization and dispersion phenomena. Indeed, within the limits of variation of the angles of incidence up to ±5° on the surface of the working mirrors (S_1, S_2) or of the end walls of the cell Q, the reflection coefficient for polarized and depolarized rays

scattered light differs so little that even with multiple reflections, as calculations showed, it does not affect the change in the intensity distribution in the spectrum of the radiation emerging from the resonator (5). Nor is it possible to explain the effect obtained by a change in the reflection coefficient for different wavelengths, which in the present case is practically absent in view of the narrowness of the spectral region used.

It should be noted that it was not possible to establish explicitly the dependence of the resonator effect on the magnitude of the degree of depolarization. However, one may state with confidence that the intensities of polarized lines are considerably more sensitive to the resonator than those of depolarized lines. This effect is especially clearly manifested when observing Raman scattering in quartz and in polymethyl methacrylate. Thus, when comparing the intensities of the Raman lines of the Si–O bond in quartz ($\nu = 466$ cm^{-1}, $\rho \sim 0.001$ (6)) in the resonator and outside it, it turned out that, when observing with the resonator, even the line could not be recorded. Along with this, for polymethyl methacrylate the C–H bond vibration $\nu = 2747$ cm^{-1}, $\rho = 0.6$ (differences in the intensity of this line in the resonator and without it within the measurement error of 5% were not found). Similar results, although less pronounced, are also observed for such classical objects as CCl_4 (217, 313, 459 cm^{-1}), chloroform (262, 366, 668 cm^{-1}), nitrobenzene (1345 cm^{-1}). Thus, the results of Table 1 should evidently be interpreted in the sense that the redistribution of energy in the Raman spectrum occurs owing to the relative weakening in the resonator of polarized lines.

Fig. 1. Diagram of the setup. Sp –DFS-4 spectrometer; L –collimator lens; S_1 and S_2 –mirrors; D_1 and D_2 –diaphragms; Hg –source of exciting light (PRK-2); Q –cell with the substance under study

Table 1

Method of observation	Benzene 1178/992	Benzene 3060/992	Toluene 1004/3051	Toluene 2920/3051	CCl_4 313/459	CCl_4 217/459
According to Vudu	0.167	0.665	0.7	0.43	0.92	0.83
I cell	0.25	0.83	0.8	0.79	–	–
I cell in interferometer	0.33	0.85	0.9	0.92	1	0.86

It was of interest to trace the influence of the base on the effect discovered. As was to be expected, with an increase in the base of the resonator the redistribution effect decreases, which is due to a decrease in the effective aperture of the setup and, consequently, in the number of "active rays." The standard base of the resonator that we used was 50 cm, which was determined by the dimensions of the illuminator; when the base was increased to 82 cm, the redistribution effect almost disappeared.

From the results of Table 1 it is seen that the resonator effect is manifested not only when observing Raman scattering with a resonator whose mirror reflection coefficient is sufficiently high (96–98%), but also with mirrors having small coefficients (10–15%), which occurs in the case of an ordinary cell with plane-parallel glass windows. In this connection it should be noted that results obtained with the use of so-called multipass cells, for example, in the case of vapors (7), cannot be directly compared with results obtained with ordinary Vudu cells.

In the literature the question of the partial coherence of Raman light has repeatedly been discussed (8). It is not excluded that some contribution to the redistribution effect

a contribution to the redistribution is made by the partial coherence of the Raman scattering, if such coherence exists. To clarify this question, we investigated the behavior of the intensity of Rayleigh scattering in the resonator and outside it. As is known, Rayleigh scattering is completely coherent. Measurements of Rayleigh scattering were carried out with CCl_4 at the mercury line 4358 Å. It turned out that in the resonator the intensity of Rayleigh scattering increased by a factor of 19. This indicates that, if one assumes that the redistribution effect is to a noticeable degree due to partial coherence, then it is possessed to a greater extent by lines with a considerable degree of depolarization.

In conclusion, we consider it our pleasant duty to express our gratitude to V. L. Broude for his interest in the work and for discussion of the results obtained.

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CITED LITERATURE

[1] I. Brandmüller, G. Moser, *Introduction to the Spectroscopy of Raman Scattering of Light*, Moscow, 1964. [2] I. I. Kondilenko, G. A. Vorob' eva, *Instruments and Experimental Techniques*, No. 2, 142 (1961). [3] L. D. Vil' ner, S. G. Rautian, A. S. Khaikin, *Optics and Spectroscopy*, 12, 437 (1962). [4] I. I. Kondilenko, P. A. Korotkov, V. L. Strizhevskii, *Optics and Spectroscopy*, 8, 471 (1960). [5] I. A. Shaikevich, Candidate' s dissertation, Kyiv, 1966. [6] J. Cabannes, Ch. Bounet, C. R. 205, 768 (1937). [7] H. L. Welsh, E. J. Stansbury et al., *J. Opt. Soc. Am.*, 45, 338 (1955). [8] G. J. Pokrowski, E. A. Gordon, *Ann. Phys.*, 4, 488 (1930); P. D. Smilova, A. I. Sokolovskaya, *Optics and Spectroscopy*, 15, 622 (1963); I. I. Kondilenko, P. A. Korotkov, V. L. Strizhevskii, Report at the XIV Conf. on Spectroscopy, Minsk, 1963.

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