

# RESONANT SPECTRA OF SPONTANEOUS RAMAN SCATTERING (SpRS) OF ANION RADICALS AND DIANIONS IN SOLUTION

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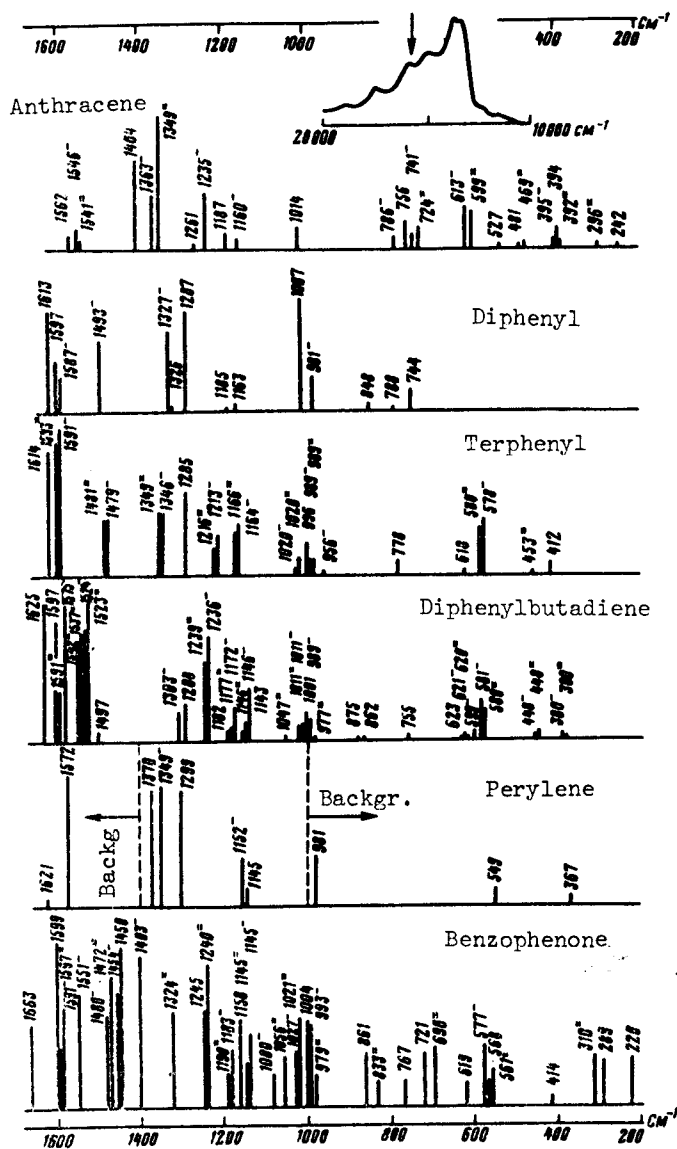
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The resonant spectra of spontaneous Raman scattering of molecular anions are investigated. A systematic shift of the spectral lines in comparison with the neutral molecules and activation of certain antisymmetrical oscillations are detected and interpreted. It is noted that such investigations are promising in connection with different problems of molecular spectroscopy.

There exists a rather extensive class of compounds, namely molecular ions, particularly anion-radicals (AR) and dianions (DA), which serve as intermediate short-lived formations and determine thereby many chemical processes. We have succeeded in realizing, for the first time, the conditions for obtaining the spontaneous Raman scattering (SpRS) spectra in such systems. The purpose of the present note is to demonstrate with concrete examples those principally new data that these experiments can contribute to spectroscopy as a whole.

The investigated AR and DA of anthracene, diphenyl, terphenyl, diphenylbutadiene, perylene, and benzophenone were obtained by the known procedure of bringing the tetrahydrofurane solutions of these compounds ( $C = 10^{-3} - 10^{-4}$  M) in contact with metallic sodium at  $20^{\circ}\text{C}$  [1]. The identification of the ions, the process of their production, and also their stability during the course of the experiment were monitored by means of the characteristic electronic absorption spectra [1, 2]. The SpRS spectra were excited with a helium-neon laser ( $\lambda = 6328 \text{ \AA}$ ). The spectral instrument was a Coderg double monochromator. The spectra of the investigated molecular ions and of the initial neutral molecules are shown schematically in the figure.

According to the concepts of quantum chemistry, the additional electrons in AR and DA fill the loose orbitals of the molecule. This should lead inevitably to a change in the other constant bonds, particularly to a decrease of the



Scheme of SpRS spectra of the investigated ions and initial molecules. The heights of the lines characterize the relative line intensities in arbitrary scale, for each spectrum. In the upper right is shown the absorption spectrum of anthracene anion-radicals. The arrow shows the position of the exciting line.

tribution to the formation of the lower free orbital of these molecules is made by the group  $C=O$  [3]. It is therefore natural to assume that the first electron is localized precisely on this orbital, and consequently the order of the bond between the carbon and oxygen atoms is decreased. This causes a vanishing of the line due to the vibrations of the carbonyl group, or a strong shift of its frequency, and also certain changes in the spectrum of the skeletal vibrations of the rings. A second electron probably influences the rings no longer indirectly but directly, and this leads to even greater changes in the entire

constant elastic multiple bonds. Accordingly, the frequencies in the vibrational spectra should also be shifted.

An analysis of the obtained data shows indeed that the joining of one electron to the initial molecule (the formation of the AR) is accompanied by just as appreciable a change in the SpRS spectrum, thus making it in individual cases difficult to compare the oscillation frequencies of the ion and of the neutral molecule without preliminary theoretical calculations. Nonetheless there is observed a general tendency for the frequency of most vibrations to decrease on going from the neutral molecule to the AR.

The joining of the second electron - the formation of the dianion - results in further spectral changes, which are sometimes no less significant than in the AR (relative to the neutral molecule). An example is benzophenone and its ions. In the case of AR and DA of terphenyl, practically identical SpRS spectra were observed, in spite of the substantial difference between their electronic absorption spectra. There is also a great similarity between the SpRS spectra of both anions of diphenylbutadiene. Consequently, the joining of a second electron to the molecule may not exert a detectable influence on its chemical bonds. In terms of quantum chemistry this means that the second electron has occupied a non-bonding orbital.

The changes in the SpRS spectra of benzophenone when its AR and DA are formed can be explained by taking into account the localization of the additional electrons. An appreciable con-

spectrum as a whole. As seen from the figure, besides the vibrations for which analogs can be found in the spectra of the corresponding neutral molecules, new vibrations are also excited sometimes in the molecular-ion spectra. For example, the AR of benzophenone is characterized by two "extra" lines in the region  $\sim 1400 - 1480 \text{ cm}^{-1}$ , the DA by one line in the region  $1240 - 1324 \text{ cm}^{-1}$ , etc. Since it is customary to assume that the symmetry of the nuclear configuration is not violated by the formation of the molecular ion, it becomes necessary to resort to the resonant specifics of the excitation of the SRS in order to explain these phenomena.

General considerations [4], the detailed theory of SpRS [5], and also the extensive experimental material, all show that the resonant conditions for spectrum excitations alter the selection rules radically. Generally speaking, fully-symmetrical vibrations should be particularly intense in SpRS [4] (just as in direct dipole transitions). It has been established, however, that the interaction ("mixing") of closely-lying electronic states, due to certain antisymmetrical vibrations, can contribute to a strong activation of the latter in the SRS as the frequency of the exciting light approaches the absorption bands of these electronic states [5]. The validity of the theoretical premises and the conclusions that follow from them were recently confirmed directly [6].

A good illustration of the applicability of these concepts to our problem can be the behavior of the lines in the region near  $600 \text{ cm}^{-1}$ , which are connected with the antisymmetrical vibrations. Being quite weak for the neutral molecules terphenyl and diphenylbutadiene ( $618$  and  $613 \text{ cm}^{-1}$ , respectively), they shift towards lower frequencies and become much stronger in the anion spectra. According to the published data, a very weak line of close frequency should appear in the anthracene spectrum. We, however, did not succeed in observing it for either dissolved or crystalline matter. In the spectrum of its anions, however, we registered lines of medium and high intensity in this region. A similar picture is sometimes observed in the case of the lines near  $1160 \text{ cm}^{-1}$ . All the mentioned anions are characterized by a complicated absorption-band structure, and scattering is excited within or near these bands. By the same token, favorable conditions are probably produced for the "mixing" of the electronic states that are grouped closely together.

It follows from all the foregoing that molecular ions, like isotopically substituted compounds, can be widely used to interpret vibrational spectra. This trend seems particularly promising because many compounds of this class can be easily studied with the aid of SpRS. On the other hand, their SpRS spectra provide unique information concerning the distinguishing features of the excited electronic states, as we attempted to show in the present article. Such experiments can also be performed on molecules in the triplet state, and constitute an independent problem.

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