THE OPTICAL PROPERTIES OF ADATOMS AND THE RESONANT RAMAN EFFECT OF MOLECULES ADSORBED ON ELECTRODES

V. V. Marinyuk, R. M. Lazorenko-Manevich,
and Ya. M. Kolotyrkin

UDC 541.13:535.375

Different explanations offered for the enhanced Raman effect (RE) which is found during the adsorption of molecules are discussed in terms of the theory of optical adatom properties. The bound electron state in the adatom–metal system which is included in this theory explains the resonant character of Raman spectrum excitation by adsorbate molecules forming a complex with metal adatoms.

It has been shown in [1-4] that the anomalously intense Raman effect (RE) of molecules adsorbed on electrodes is found only for adsorbate molecules associated with metal adatoms. A similar viewpoint is expressed in [5-7]. According to [1-7], the anomalously high intensity of the adsorbate's Raman spectrum is due to a resonant RE (RRE) caused by optical absorption in the metal–adatom system. Such absorption was directly observed in [2, 4] in electroreflectance (ER) spectra of silver, and apparently it also was observed in [8], even though a different interpretation of the ER spectra was offered there. The energy of the absorption band responsible for the RRE is about 1.9 eV, with a half-width of 0.2 to 0.3 eV [4]. Two explanations exist in the literature for absorption in the adatom–metal system and, accordingly, for the origin of RRE during adsorption. It is proposed in [1-4] that the absorption band arises owing to optical excitation of an electron from a quasilevel in the adatom to free states in the metal's conduction band. If now an adsorbate molecule forms a complex with the adatom by partial charge transfer of an adatom electron to the adsorbed molecule [3], then a strong modulation of the adatom–metal transition probability by vibrations of the molecule becomes possible, and this should become apparent in RRE. According to [5-7], the lattice symmetry is reduced in the presence of an adatom, hence optical intraband transitions in the metal are allowed, and this in turn gives rise to absorption in the adatom–metal system. The resonant enhancement of the adsorbate molecule's Raman spectrum can in this case be described, according to [7], by an expression of the form [9]:

$$\sigma_v(\omega) \sim \left| \sum_{ij} \frac{\langle 0|H_{ep}|j\rangle\langle 1,j|H_{ev}|0,i\rangle\langle i|H_{ep}|0\rangle}{(\omega-\omega_v-\omega_j-i\gamma_j)(\omega-\omega_i-i\gamma_i)} \right|^2 \qquad (1)$$

where $\sigma_V(\omega)$ is the scattering cross section of the light, H_{ev} is the Hamiltonian describing interaction of metal electrons with adsorbate molecule vibrations of frequency ω_V, H_{ep} is the Hamiltonian of electron–phonon interaction, ω is the frequency of the incident light, $|0\rangle$ is the electron's initial state, $|i\rangle$ and $|j\rangle$ are their attenuation constants, γ_i and γ_j are the energies of transitions $\hbar\omega_i$ and $\hbar\omega_j$ are the energies of transitions $0 \rightarrow i$ and $0 \rightarrow j$, respectively, and 0 and 1 are the vibrational ground state and excited state, respectively. Because of the law of conservation of electron momentum, matrix elements H_{ep} are zero in the absence of adatoms. In the presence of a symmetry-reducing adatom, transitions with arbitrary energies $\hbar\omega_i$ becomes possible according to [7], so that RRE should be seen at all wavelengths of the exciting light. The increase in the adsorbate's Raman intensity with decreasing ω which is seen in the experiments remains unexplained from this position. It must also be pointed out that in [5-7], adatoms merely lower the lattice symmetry. But symmetry is lowered to exactly the same extent in the presence of other point defects (vacancies, kinked steps), which according to [5-7] should also cause RRE. However, the experimental data of [4] indicate that precisely the adatoms are responsible for RRE.

On the mere basis of experimental data, it is difficult to reach specific conclusions as to the nature of the absorption band responsible for anomalously intense RE. Recent theoretical studies of the effect of adatoms on the electronic structure and optical properties of metal surfaces [10-12] are of particular interest in this

---

L. Ya. Karpov Scientific-Research Physicochemical Institute, Moscow. Translated from Élektrokhimiya, Vol. 18, No. 3, pp. 307-311, March, 1982. Original article submitted February 2, 1981.

connection. In these papers the interaction of conduction electrons with an adatom is discussed in terms of electron scattering at the adatom potential. It was shown that the scattering matrix has a pole at the metal electron energy which equals the energy of the bound adatom state. This result at once reveals the bound state as a special feature of electronic structure of the adatom–metal system which is not taken into account in [5-7]. According to [5-7], metal electrons can absorb light in intraband transitions, only when the momentum is not conserved. This evidently is the case only for electrons scattered at an adatom. According to [10-12], such scattering is most likely for electrons having energies close to the bound adatom state. For bound adatom states below the Fermi level (as should exist for the silver adatoms on silver), the most intense absorption of light should occur at photon energies equal to or larger than the transition energy from the adatom's quasilevel to the metal's Fermi level. Considering that electronic states of the metal having an energy close to the adatom's quasilevel are localized in part at the adatom [10-12], while excited states having an energy higher than the Fermi level are localized in the metal, one apparently can interpret the absorption band observed in [2, 4, 8] as a charge-transfer band in the adatom–metal system. Thus, the mechanism proposed in [5-7] leads to a result fully in accord with the model of [1-4] when the theory of [10-12] is taken into account. It had been shown in [10-12], on the other hand, that the level of an isolated atom during adsorption is broadened, and converted to a resonant state that can decompose into states in the bulk and surface bands of the metal. In other words, the adatom electron is partly delocalized, and unlike [1-4], the transitions in the entire electronic adatom–metal system [10-12] must be considered when describing the optical properties of a metal in the presence of adatoms. One can see that from the theoretical position of [10-12], the models of [1-4] and [5-7] are not inconsistent, but they stress separate aspects of the complicated adatom–metal interaction.

Let us examine from the position of [10-12] the behavior of the resonant Raman spectra of molecules adsorbed on electrodes. Their basic features are as follows: (a) resonant character of the spectral intensity as a function of frequency, ω, of the exciting light [3, 8, 13, 14]; (b) a dependence of the intensity ratios of different lines on ω [14]; (c) a dependence of the intensity ratio, I_s/I_{as}, of Stokes and anti-Stokes lines on ω [3, 4]; (d) enhancement of practically all lines of the molecule's vibrational spectrum during adsorption, including lines which under ordinary conditions are active only in the IR spectra [15]; and (e) an enhancement of spectral intensity during adsorption by six orders of magnitude.

For the discussion we shall use relation (1), and only point out that electronic states $|0\rangle$, $|i\rangle$, and $|j\rangle$ are described by wave functions which in [12] have been calculated while allowing for the effect of metal adatoms. If we assume, as in [9], that matrix elements $\langle 1, j\,|\,H_{ev}\,|0, i\rangle$ are independent of i and j we have

$$\sigma_v(\omega)\sim|\alpha(\omega)\alpha(\omega\pm\omega_v)|^2. \tag{2}$$

The plus and minus sign in (2) refer to anti-Stokes and Stokes lines, respectively. It must be pointed out that relation (2) can be obtained, under appropriate assumptions concerning the form of the matrix elements, even from expressions more general than (1). One can see that the dependence of σ_V on ω should qualitatively duplicate the frequency dependence of polarizability α of the adatom–metal system; the imaginary part of this function is described, according to [12], by the relation

$$\alpha''(\omega)=\frac{\pi}{3}\frac{e^2}{m\omega^4\hbar^2}\frac{|E_0+\Lambda+\hbar\omega|^{3/2}}{|E_0+\Lambda|^{3/2}}\Gamma_{l=1}(E_0+\Lambda+\hbar\omega)\left[\operatorname{arc\,tan}\frac{E_F-E_0-\Lambda}{\Gamma}-\operatorname{arc\,tan}\frac{E_F-E_0-\Lambda-\hbar\omega}{\Gamma}\right], \tag{3}$$

where E_0 is the energy of the isolated atom's highest occupied level, which upon adsorption is displaced by Λ and broadened to a width Γ, $\Gamma_{l=1}(E_0+\Lambda+\hbar\omega)$ is the width of the excited electronic state, and E_F is the energy of the Fermi level. (We do not report the unwieldy expression for $\alpha'(\omega)$). It had been shown in [12] that function $\alpha''(\omega)$ has a maximum at $\hbar\omega=\hbar\omega_p=E_F-E_0-\Lambda$, i.e., at the energy corresponding to the transition from the adatom to the metal's Fermi level. Function $\alpha'(\omega)$ according to [12] also has structure close to this energy. Thus, the results listed under (a) are qualitatively explained with the aid of theory [10-12]. We point out that the assumed constancy of matrix elements H_{ev} cannot influence this result. In fact, electron–vibration interaction should only be strong when there is appreciable overlap between the wave functions of the conduction electrons and the nuclear wave functions of the adsorbate molecule. This condition basically holds only for electrons with energy $E_0+\Lambda$ partly localized at the adatom, i.e., the matrix elements H_{ev} are largest when $|i\rangle$ and $|j\rangle$ are the excited states of these electrons. One can assume, therefore, that the resonant character of $\sigma_V(\omega)$ is more pronounced than that of $\alpha''(\omega)$. It is interesting to note that function $\alpha''(\omega)$ ought to be asymmetric relative to ω_p [12]. This evidently is due to the fact that upon excitation with light of frequencies $\omega>\omega_p$ one has strict resonance with unoccupied states in the conduction band, but this is not the case for $\omega<\omega_p$. The experimental $\sigma_V(\omega)$ [8, 13, 16] so far do not provide a clear answer as to their asymmetry, since a single point is reported for $\omega<\omega_p$ in [16], while no measurements at all were performed in this region owing to experimental limitations in [8, 13]. We believe that the discovery of asymmetry in spectra of $\sigma_V(\omega)$

would be a very important argument for the application of theory [10-12] in explaining adsorption-induced RRE. We add here that (2) also yields the dependence of I_s/I_{as} on ω listed under (c).

The ω-dependence of line intensity ratios in the adsorbate's RRE spectrum that was mentioned under (b) can be explained as follows. The region where the adatom electron is localized is of the same size range as the adsorbate molecule; therefore, matrix elements $\langle 1, j | H_{ev} | 0, i \rangle$ in (1) which characterize the interaction of excited adatom states with vibrations of the molecule should depend on the form of the given vibration. Hence the shape of the curves of $\sigma_V(\omega)$ determined by the sum in (1) also should be different for different vibrations.

We point out that the line intensity ratios in the Raman spectrum of a molecule may substantially change upon adsorption, since the intensity of this spectrum is determined by interaction of the molecular vibrations with the metal electrons, and not with the electrons of the molecule itself. The interaction of molecular vibrations with the electrons of the adatom—metal system evidently can be regarded as the result of modulation of adatom potential V_a [10-12] (at which the metal electrons are scattered) by the molecular vibrations. On the assumption that a charge-transfer complex is formed between the adsorbate molecule and the adatom [3], the modulation of potential V_a by the molecular vibrations basically should be seen as a modulation of the degree of charge transfer between adatom and adsorbate. In view of the important asymmetry of the adsorbate—adatom—metal system, this charge transfer apparently can be modulated sufficiently strongly by many kinds of vibration. The strongest modulation of charge transfer ought to occur in the case of IR-active vibrations modulating the molecule's dipole moment, and this explains the observations reported under (d).

Coming to (e) we shall use relation (3) to estimate the RRE spectrum intensity of an adsorbate interacting with an adatom. We find $\alpha'' \approx 6 \cdot 10^{-23}$ cm^3 when substituting into (3) the parameters of the absorption band observed in ER spectra [4], and assuming that the width of the excited state $\Gamma_{l=1} \approx 1$ eV. The scattering cross section, σ, for the Rayleigh line which is given by $\sigma = 8\pi\omega^4\alpha^2/3c^4$ will amount to about $3 \cdot 10^{-24}$ cm^2. Considering that usually the intensities of Raman lines are about 2 orders of magnitude lower than those of the Rayleigh line [17] we obtain $\sigma_V \approx 3 \cdot 10^{-26}$ cm^2. The scattering cross section in the usual, vibrational RE is on the order of 10^{-29} cm^2 when it is excited with red light [18]. Thus, RRE by adsorbate molecules interacting with adatoms will produce an adsorption-induced enhancement of the spectrum of no more than three to four orders of magnitude. One can see that this figure is markedly lower than the intensity increase of the Raman spectra found upon adsorption in the experiments. We point out in this connection that a similar conclusion is reached also from an estimate of oscillator strength of the electronic transition that would be needed to produce such an increase [2].

In addition to the mechanism of [1-4], a number of papers suggest enhanced intensity of the exciting electromagnetic field close to the metal surface as a reason for anomalously intense RE. This enhancement is possible when a surface plasmon is excited on a rough surface [13], or when intrinsic plasma oscillations are excited in metal particles having a size much smaller than the wavelength of the light, which according to [19] are present on the surface. Presently the situation is such that the bulk of the data (the behavior of I_s/I_{as}, the ω-dependence of the line intensity ratios of the Raman spectrum) can be explained only in terms of RRE arising upon adsorption. Results such as adsorption-enhanced spectrum intensity and its ω-dependence can be explained qualitatively with any of the hypotheses, but in a number of cases one must adduce rather artificial arguments. It was discovered in [20], on the other hand, that a certain enhancement of a molecule's Raman spectrum will result even when it is 50 Å away from the surface. This result evidently can only be explained in terms of models allowing for plasmon excitation.

It is very important to realize, however, that neither RRE nor theories of [19, 20] seem able to explain the extent (six orders of magnitude) of Raman spectrum enhancement found, in particular, upon the adsorption of pyridine. This argument, and the data reported above, clearly demonstrate that the overall effect of anomalously intense RE must be the result, both of RRE and of enhanced intensity of the exciting field close to the metal surface. The importance of the first factor is determined by the number of metal adatoms and by the interaction of adsorbate molecules with them. The importance of the second factor is determined by the degree of surface roughness and, probably, by illumination geometry. It seems that the relative importance of these factors to Raman spectrum enhancement can be different in different adsorbate—metal systems, so that some authors are led to hypothesize RRE, while others are induced to conclude that surface plasmons are decisive. For pyridine in particular, one also must reckon with a possible Raman enhancement owing to correlation of the molecular vibrations at high degrees of coverage [2].

The model discussed in the present work can be generalized to include a wider range of adsorbed species and adsorption sites. It has been shown above that an adatom on one hand gives rise to intense light absorption in intraband transitions, but on the other hand it is an effective adsorption site mediating sufficiently strong interaction of the molecular vibrations with the metal electrons. Yet optical intraband transitions – this has been pointed out before – can occur also during electron scattering at other point defects of the metal surface, even though the intensity of these transitions may be much lower than that found in the case of adatoms. Moreover, upon chemisorption the adsorbed molecule itself is a site for electron scattering, and hence can play the same part as an adatom. It is obvious that in all these cases, the Raman intensity will also be determined by the degree of interaction of the molecular vibrations with the metal electrons. One can conclude, therefore, that adsorption always will lead to a certain increase in the molecule's Raman spectrum intensity. The magnitude of this increase ought to depend, both on the adsorption properties of the surface (the presence of adatoms and other defects) and on the type of adsorption bond existing between the molecule and the metal.

In conclusion the authors express their gratitude to A. M. Brodskii and R. R. Dogonadze for discussing the results and giving useful comments.

LITERATURE CITED

1. R. M. Lazorenko-Manevich, V. V. Marinyuk, and Ya. M. Kolotyrkin, "The mechanism of anomalously intense Raman scattering during adsorption on electrodes," Dokl. Akad. Nauk SSSR, 244, 641 (1979).
2. V. V. Marinyuk and R. M. Lazorenko-Manevich, "The mechanism of anomalously intense Raman scattering during adsorption on electrodes," Élektrokhimiya, 16, 332 (1980).
3. V. V. Marinyuk, R. M. Lazorenko-Manevich, and Ya. M. Kolotyrkin, "Nature of the interaction of adsorbate molecules with metal adatoms," J. Electroanal. Chem., 110, 111 (1980).
4. V. V. Marinyuk, R. M. Lazorenko-Manevich, and Ya. M. Kolotyrkin, "The importance of metal adatoms in the development of a resonant Raman effect of pyridine adsorbed on silver," Dokl. Akad. Nauk SSSR, 253, 155 (1980).
5. A. Otto, J. Timper, J. Billmann, G. Kovacs, and I. Pockrand, "Surface roughness induced electronic Raman scattering," Surf. Sci., 92, L55 (1980).
6. A. Otto, J. Timper, J. Billmann, and I. Pockrand, "Enhanced inelastic light scattering from metal electrodes caused by adatoms," Phys. Rev. Lett., 45, 46 (1980).
7. J. Billmann, G. Kovacs, and A. Otto, "Enhanced Raman effect from cyanide adsorbed on a silver electrode," Surf. Sci., 92, 153 (1980).
8. B. Pettinger, U. Wenning, and D. M. Kolb, Raman and reflectance spectroscopy of pyridine adsorbed on single crystal silver electrodes," Ber. Bunsenges. Phys. Chem., 82, 1326 (1978).
9. R. M. Martin and L. M. Falicov, "Resonant Raman scattering," in: Light Scattering in Solids [Topics in Applied Physics Series, Vol. 8], M. Cardona, ed., Springer, Berlin (1975).
10. A. M. Brodskii and M. I. Urbakh, "Adsorption-induced changes of electron levels," Phys. Sol., 76, 93 (1976).
11. A. M. Brodskii and M. I. Urbakh, "Influence of isolated adatoms on surface electronic states," Surf. Sci., 66, 463 (1977).
12. A. M. Brodskii and M. I. Urbakh, "On the dependence of light reflection from metals on adatom characteristics," Phys. Stat. Sol., 83, 633 (1977).
13. J. A. Creighton, M. G. Albrecht, R. E. Hester, and J. A. D. Matthew, "The dependence of the intensity of Raman bands of pyridine at a silver electrode on the wavelength of excitation," Chem. Phys. Lett., 55, 55 (1978).
14. V. V. Marinyuk, R. M. Lazorenko-Manevich, and Ya. M. Kolotyrkin, "Resonant Raman scattering of pyridine adsorbed on silver," Élektrokhimiya, 14, 1019 (1978).
15. A. Otto, "Raman spectra of CN^- adsorbed at a silver surface," Surf. Sci., 75, L382 (1978).
16. A. Otto, "Surface-enhanced Raman scattering (SERS) – what do we know?", Proc. 6th Solid–Vacuum Interface Conf., Delft, The Netherlands, May 7 to 9, 1980.
17. T. R. Gilson and P. J. Hendra, Laser Raman Spectroscopy. A Survey of Interest Primarily to Chemists, Wiley-Interscience, New York (1970).
18. T. C. Damen, R. C. C. Leite, and S. P. S. Porto, "Angular dependence of the Raman scattering from benzene excited by the He–Ne cw laser," Phys. Rev. Lett., 14, 9 (1964).
19. M. Moskovits, "Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals," J. Chem. Phys., 69, 4159 (1978).
20. D. A. Zwemer, C. V. Shank, and J. E. Rowe, "Surface-enhanced Raman scattering as a function of molecule–surface separation," Chem. Phys. Lett., 73, 201 (1980).