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Importance of Vibrational Coupling in the Vibrational Frequency Shifts of Diatomic Molecules Caused by Adsorption

The vibrational frequency shift of a diatomic molecule such as CO or NO on adsorption is discussed in terms of the coupling between the two vibrations of an admolecule and of a metal–admolecule bond. The coupling induces a significant degree of apparent high-frequency shift of the admolecule vibration compatible with the observed value in certain cases.

Adsorption of a diatomic molecule such as CO or NO on metal or metal oxide surfaces has been studied by means of the infrared absorption technique to elucidate the nature of bonding in the admolecule and of the interaction with adsorbate. The observed frequency shift in diatomics has often been interpreted as only due to the change in the bond strength in diatomics upon adsorption. For example, in the case of CO adsorption on metal surfaces, the C–O stretching vibration shifts to lower frequency because of the back-donation of electrons from the metal to the antibonding 2π orbital of CO (*1*). On the other hand, for CO adsorbed on oxide surfaces, the C–O stretching vibration has often been observed at a higher frequency than that of gaseous CO. The observed high-frequency shift was explained by another electronic configuration in CO admolecule such as CO^+, by the dipole–dipole interaction between CO and induced dipole near the catalyst surface, and by other factors (*2*).

It should be noted that the simple classical treatment of the coupling between the vibration of the admolecule and that of the adsorbate–adsorbent bond predicts the shift of the vibrational frequency even in the case where there is no change in the bond strength in the admolecule. Since this effect seems to have been sometimes overlooked, we will show in this note how the simple treatment of coupling predicts the frequency shift on adsorption and how one can deduce the real change in the bonding nature from the observed vibrational frequencies.

We now consider a simple model for adsorption of a diatomic molecule XY on a surface metal atom M where we assume the formation of a linear triatomic molecule as shown below:

$$\begin{array}{c} k_2 \ k_1 \\ \text{M–X–Y} \\ m_3 \ m_2 \ m_1 \end{array}$$

where k_1 and k_2 are the force constants of the XY and MX bonds, respectively, and m_i is the atomic mass of each atom. One can introduce vibrational frequencies ν_{1o} and ν_{2o} of the diatomics XY and MX with the force constants k_1 and k_2, respectively. When the admolecule is constructed, the two vibrations are coupled with each other giving rise to the frequencies shifted to ν_{1s} and ν_{2s} (*3*), which are the frequencies of the two stretching vibrational modes in the triatomic molecule MXY and should be compared with the observed vibrational frequencies of the adsorbate–adsorbent

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TABLE 1

Calculation of Frequency Shifts in the ν_{CO} Band Caused by Adsorption of CO on Cr_2O_3

Frequency shift (cm^{-1})			
Assumed		Calculated	
ν_{1o}	ν_{2s}	ν_{1s}	ν_{2o}
2143[a]	250	2156	343
	300	2162	412
	350	2169	483
	400	2177	555
	450	2187	627
	500	2198	701
	550	2211	775

[a] Observed value of gaseous CO molecule.

system. They are given by equations:

$$4\pi^2(\nu_{1s}^2 + \nu_{2s}^2) = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)k_1 + \left(\frac{1}{m_2} + \frac{1}{m_3}\right)k_2 = 4\pi^2(\nu_{1o}^2 + \nu_{2o}^2) \qquad (1)$$

$$16\pi^4\nu_{1s}^2\nu_{2s}^2 = \frac{m_1 + m_2 + m_3}{m_1m_2m_3}k_1k_2. \qquad (2)$$

Then, using the relation

$$16\pi^4\nu_{1o}^2\nu_{2o}^2 = \frac{m_1 + m_2}{m_1m_2}k_1\frac{m_2 + m_3}{m_2m_3}k_2 \qquad (3)$$

which follows from the definition of ν_{1o} and ν_{2o}, we get the following equation describing the frequency shift

$$(\nu_{1s}^2 - \nu_{2s}^2)^2 - (\nu_{1o}^2 - \nu_{2o}^2)^2 = \frac{4m_1m_3}{(m_1 + m_2)(m_2 + m_3)}\nu_{1o}^2\nu_{2o}^2. \qquad (4)$$

Since Eq. (4) is always positive, an important conclusion drawn from the above treatment is that the formation of the admolecule must cause a high-frequency shift in the higher-frequency band and a low-frequency shift in the lower one. Accordingly, even if the bond strength, i.e., force constant, in the diatomic molecule does not change upon adsorption, a high-frequency shift in the corresponding vibration should always be expected, taking $\nu_{1o} > \nu_{2o}$ for granted.

When ν_{1s} and ν_{2s} are determined experimentally, one can calculate ν_{1o} from Eqs. (1) and (4) and then compare it with the vibrational frequency of the gaseous diatomic molecule. It is apparent that the measurement of ν_{2s} as well as ν_{1s} is of vital importance to deduce the real change in the bond strength of a diatomic molecule upon adsorption. In the case that ν_{1o} is estimated at a reasonable value, ν_{1s} can be calculated as a function of ν_{2s} and can be compared with the observed frequency.

Let us consider an example of the model for CO adsorption on a transition metal atom of its oxide where the CO molecule is adsorbed via electron donation from 5σ nonbonding or slightly antibonding orbital of CO to the vacant d orbital of the transition metal atom. To be specific, we consider CO adsorption on Cr_2O_3. Assuming $\nu_{1o} = \nu_{CO(gas)}$, $m_3 = 52$ amu for Cr, and ν_{2s} to be certain frequencies around the observed value of metal–carbon stretching vibration of CO adsorbed on transition metal surfaces (*5*), we obtain ν_{1s} as shown in Table 1. The calculated shift of ν_{1s} from $\nu_{CO(gas)}$ is comparable with the observed ν_{1s} range (*4*). This relation explains reasonably the frequency shift due to the change in the coverage of CO. That is, the lower the coverage, the larger is the high-frequency shift in the carbon–oxygen stretching vibration, provided that the interaction between adsorbate and adsorbent, i.e., ν_{2o}, increases with decreasing coverage.

Another example is CO adsorption on Ni metal where both ν_{1s} and ν_{2s} are known. The frequencies of the C–O stretching vibrations were reported to be 2080 and 1940 cm^{-1} for CO adsorbed on a Ni surface, where the Ni–C stretching frequency was observed at 435 cm^{-1} (*5*). They were assigned, respectively, to the linear CO and to the bridged CO, based on the comparison with the ir spectra of the carbonyl complexes (*6*). Since the linear configuration is well-fitted to our treatment, we calculate ν_{1o} and ν_{2o} using the observed value of $\nu_{1s} = 2080$ cm^{-1}, $\nu_{2s} = 435$ cm^{-1}, and $m_3 = 59$ amu for Ni. They are 2034 and 614 cm^{-1}, respectively. Accordingly, it is suggested that the true change in the C–O bond strength upon adsorption corresponds not to 63 cm^{-1}, the difference between $\nu_{\mathrm{CO(gas)}}$ and ν_{1s}, but to 110 cm^{-1}, the difference between $\nu_{\mathrm{CO(gas)}}$ and ν_{1o}.

The above consideration of the vibrational coupling shows that the observed frequency shift should not be attributed only to the change in the bond strength in admolecules. When the bonding in admolecules becomes stronger on adsorption, one would observe a larger high-frequency shift than that corresponding to a change in the bonding. Even when it is a little weakened, a high-frequency shift might be observed as well, owing to vibrational coupling. For a low-frequency shift, one would underestimate the change in bonding without the consideration of vibrational coupling. Essentially the same consideration should be taken into account in discussing the vibration of adsorbed molecules in general, including that of polyatomic molecules.

REFERENCES

1. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," Wiley, New York, 1972.
2. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.
3. Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules." Van Nostrand, New York, 1945.
4. Zecchina, A., Coluccia, S., Guglielminotti E., and Ghiotti, G., *J. Phys. Chem.* **75**, 2774 (1971).
5. Blyholder, G., *in* "Proceedings. 3rd International Congress on Catalysis, July, 1964," Amsterdam, p. 655 North-Holland, Amsterdam; Andersson, S., *Solid State Commun.* 21, 75 (1977); Froitzheim, H., Hopster, H., Ibach, H., and Lehwald, S., *Appl. Phys.* **13**, 147 (1977).
6. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds," 2nd. Ed. Wiley, New York, 1970.

TADASHI OKAWA
MITSUYUKI SOMA
HIROSHI BANDOW
KIYOSHI UCHIDA

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

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