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The Infrared Spectra of Carbon Dioxide Intermedions

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The assignment of certain bands reported in the infrared spectra of carbon dioxide in contact with adsorbents indicates the discovery of CO_2 intermedions. The adsorbents contained nickel, zinc oxide, or sodium chloride. Equations are derived relating the vibrational frequencies to the numbers of valence electrons for each of the three normal vibrations of CO_2. According to these equations, the vibrational frequencies of the adsorbed CO_2 intermedions correspond to nonintegral numbers of electrons, that is, numbers composed of an integer and a fraction. These fractions, known as "polarization fractions," are considered to be constants characteristic of each metal. The fractions observed for each adsorbent are 0.32 for zinc, and 0.90 for sodium. The bands reported for CO_2 on sodium chloride permitted an analysis which suggests that some of the chemisorbed CO_2 intermedions are oriented parallel with the surface while others are perpendicular. These species have vibrational frequencies which correspond to the acceptance of nearly two electrons, forming an approximate $(CO_2)^{2-}$ ion. Polarization of this magnitude changes the internuclear angle from 180 to 60°. Yet these adsorbates seem to be so weakly bonded to the surface that there is evidence of their rotation.

INTRODUCTION

Certain absorption bands in the infrared spectra of carbon monoxide in contact with adsorbents containing copper and cobalt were attributed to species known as intermedions (*1*). The species producing these bands do not appear to be chemisorbed since they are weakly bonded to the surface and readily removed by evacuation. Yet they cannot be considered physically adsorbed since their vibrational frequencies may be quite different from gaseous CO. A significant electronic polarization along with such weak bonding might be the result of a dipole–induced-dipole interaction between adsorbate and surface without electron sharing or transfer. Despite the possibility that electron transfer does not occur during the formation of intermedions, it is useful to express the mangnitude of the polarization of the adsorbate in terms of an apparent change in numbers of valence electrons (*2*). In the case of CO, an equation has been derived relating the vibrational frequencies of CO intermedions to their numbers of valence electrons. Since the vibrational frequencies of CO intermedions are between those of the neutral CO molecule and its ions, the corresponding numbers of electrons are nonintegral. The integer of the nonintegral number (of electrons) depends on the oxidation state of the metal component of the adsorbent compound. The fractional part of this nonintegral number (of electrons) is a unique constant of that metal. It is referred to as the "polarization fraction" since it is the fractional part of the polarization experienced by chemisorbed intermedions on adsorbents containing that metal.

Carbon monoxide was the first molecule whose intermedions have been detected. In some part, this unique position of CO is related to the high extinction coefficient of its infrared bands. If intermedions are present in relatively low concentrations on the surfaces of adsorbents, those which produce the more intense adsorption bands would be the first detected. The following interpretations of infrared bands reported for carbon dioxide in contact with adsorbents indicate that CO_2 intermedions may now have been detected also.

DISCUSSION

Spectra obtained during the preparation of NiO from $NiCO_3$ are reported by Filimonov (*3*). The infrared spectra of the nickel oxide showed absorption maxima at 1635, 1480, 1390, 1125, and 1030 cm^{-1}. The band at 1635 cm^{-1} vanished when the sample was evacuated at room temperature. The other bands were removed only by evacuation at elevated temperatures. The weak bonding of the species producing the band at 1635 cm^{-1} is characteristic of intermedions.

This cannot be a CO intermedion. The polarization fraction of nickel is 0.857. Therefore, on adsorbents containing nickel or nickel compounds, CO intermedions will have vibrational frequencies which correspond to 8.857, 9.857, 10.857, and/or 11.857 electrons. The equation relating vibration frequency ν and numbers of electrons E for CO was derived in a previous paper (*1*). It is

$$[\nu(\mathrm{CO}) - 2269.96][E(\mathrm{CO}) - 12.1182] = 268.309\ \mathrm{cm}^{-1}. \quad (1)$$

The CO intermedions which correspond to these numbers of electrons have vibration frequencies of 2188, 2151, 2057, and 1242 cm^{-1}.

The band at 1635 cm^{-1} observed during the decomposition of $NiCO_3$ may be due to the ν_3 vibration of a CO_2 intermedion. Since the unsymmetric stretch of CO_2 is predominantly a C-to-O stretching motion, there may be some similarity in the equation of the ν_3 vibration of CO_2 intermedions and Eq. (1) of CO intermedions. The values of ν_3 of CO_2 intermedions in Table 1 are proposed as similar to the corresponding ones for CO intermedions. The equation of the right hyperbola relating the three values of ν_3CO_2 in Table 1 is

$$[\nu_3(\mathrm{CO_2}) - 2431.1][\mathrm{E}(\mathrm{CO_2}) - 18.070] = 170.18\ \mathrm{cm}^{-1} \quad (2)$$

This equation may be tested by calculating the numbers of electrons which correspond to the vibrational frequencies of bands attributed to adsorbed CO_2. The equation is supported if the numbers of electrons are nonintegral with fractions which are the polarization fraction of the metallic component of the adsorbent compound. If the polarization fraction of the metal is not known, then two or more adsorbates are considered intermedions if they have vibrational frequencies which correspond to numbers of electrons with different integers but the same fraction. This fraction is then considered to be the polarization fraction of the metallic component of the adsorbent.

Taylor and Amberg (*5*) report that the addition of CO to a zinc oxide adsorbent at 25°C produced a band in the infrared spectrum at 2174 cm^{-1}. On standing, the peak shifted to 2198 cm^{-1}. Both bands were readily removed by evacuation. When CO was admitted to zinc oxide at 155°C, no band formed at 2174 cm^{-1}. However, in some cases a small peak was observed at 2198 cm^{-1}. If the oxidation of CO to CO_2 is slow at 25 and rapid at 155°C, the bands at 2174 and 2198 cm^{-1} could be due to CO and CO_2 adsorbates, respectively. Ac-

TABLE 1
CORRESPONDING CO AND CO_2 INTERMEDIONS

$\nu(\mathrm{CO})^{10} = 2143.27\ \mathrm{cm}^{-1}$ (*4*)	$\nu_3(\mathrm{CO_2})^{16} = 2349.3\ \mathrm{cm}^{-1}$	The neutral molecule
$\nu(\mathrm{CO})^{10.857} = 2057.22$		The higher frequency negative intermedion on nickel
$\nu(\mathrm{CO})^{11.857} = 1242.74$	$\nu_3(\mathrm{CO_2})^{17.857} = 1635$	The lower frequency negative intermedion on nickel
$\nu(\mathrm{CO})^{12} = 0.0$	$\nu_3(\mathrm{CO_2})^{18} = 0.0$	The −2 ion

cording to Eq. (1), 2174 cm^{-1} corresponds to a CO intermedion with 9.322 valence electrons. According to Eq. (2), 2198 cm^{-1} corresponds to the ν_3 vibration of a CO_2 intermedion with 17.34 electrons. The agreement, within 0.02, of the fractions of the numbers of electrons calculated for CO and CO_2 intermedions on zinc oxide not only supports Eq. (2) for CO_2 intermedions but also indicates that the polarization fraction of zinc is 0.32. (The fraction for the CO intermedion is chosen as the polarization fraction since the equation of CO intermedions is considered more accurate than Eq. (2) for CO_2 intermedions.)

Kozirovsky and Folman (*6*) report the spectra of CO_2 on NaCl. In addition to the absorption band at 2350 cm^{-1} for gaseous CO_2, they observed bands at 2288, 1379 and in the 600 cm^{-1} region. According to Eq. (2), a vibrational frequency of 2288 cm^{-1} corresponds to $\nu_3(CO_2)^{16.89}$ and a vibrational frequency of 1379 cm^{-1} corresponds to $\nu_3(CO_2)^{17.91}$. The similarity of these fractions suggests that these bands are due to chemisorbed CO_2 intermedions and indicates that the polarization fraction of sodium may be approximately 0.90.

According to this interpretation, the four bands at 658.3, 647.2, 630.9, and 629.3 cm^{-1} cannot be due to the ν_3 vibration of chemisorbed CO_2 intermedions. These bands might be due to the ν_2 vibration or even the ν_1 vibration if it has become infrared active as a result of chemisorption. The equations relating ν and E for the ν_1 and ν_2 vibrations of CO_2 may be derived from the values of 1336.9 and 667.3 cm^{-1} for these vibrations for the neutral molecule and the following two assumptions: It is assumed that all three vibrations become zero when the molecule dissociates at 18 valence electrons; it is assumed that the right hyperbolas describing ν and E for each of the three fundamental vibrations have the same curvature k. The two equations derived from these assumptions are:

$$[\nu_1(CO_2) - 1418.2][E(CO_2) - 18.120] = 170.18\ cm^{-1} \quad (3)$$

$$[\nu_2(CO_2) - 743.1][E(CO_2) - 18.229] = 170.18\ cm^{-1} \quad (4)$$

On the basis of 0.90 as the polarization fraction of sodium, the ν_2 vibrations of the two chemisorbed CO_2 intermedions would be

$$\nu_2 CO_2{}^{16.90} = 615.0\ cm^{-1} \quad (5)$$

$$\nu_2 CO_2{}^{16.90} = 225.8\ cm^{-1} \quad (6)$$

The bands reported in the 600 cm^{-1} region are at frequencies that are too high to correspond even to $\nu_2 CO_2{}^{16.90}$.

The other possibility is that ν_1, the symmetrical stretch, might become infrared active for these CO_2 intermedions. This vibration is infrared inactive in the gas phase since CO_2 is linear with $D_{\infty h}$ symmetry. According to Walsh (*7*) the addition of electrons to CO_2 is expected to change its structure from linear to bent. The change from $D_{\infty h}$ to C_{2v} symmetry would make the ν_1 vibration infrared active. According to Eq. (3), the four bands correspond to the ν_1 vibrations of the following CO_2 intermedions,

$$\nu_1 CO_2{}^{17.896} = 658.3\ cm^{-1} \quad (7)$$

$$\nu_1 CO_2{}^{17.899} = 657.2 \quad (8)$$

$$\nu_1 CO_2{}^{17.904} = 630.9 \quad (9)$$

$$\nu_1 CO_2{}^{17.904} = 629.3 \quad (10)$$

The cluster of numbers of electrons about 17.90 is most encouraging. However, one band would have been sufficient.

Two bands corresponding to $\nu_1 CO_2{}^{17.90}$ could be due to a splitting of this vibration depending on whether the adsorbate is oriented parallel or perpendicular to the surface. Evidence for orientation of adsorbed species parallel and perpendicular to the surface has been given by Yates and Lucchesi (*8*) in their study of the infrared spectra of chemisorbed acetylene. When Kozirovsky and Folman (*6*) varied the surface coverage, the four bands changed in intensity as if they were paired. These bands were described (*6*) as two doublets with maxima at 658.3 and 629.3 cm^{-1}; 647.2 and 630.9 cm^{-1}. If these CO_2 intermedions are limited to two orientations with respect to the surface, yet are free to rotate, each pair of bands might be branches of a rotation–vibration envelope. Carter *et al.* (*9*) found evidence of adsorbate rotation in an infrared study of ethylene on zeolites.

If the four bands in the 600 cm^{-1} region are pairs of vibration–rotation envelopes produced by two orientations of CO_2 intermedions, some approximate deductions may be made concerning the internuclear angle. A bent CO_2 is a planar unsymmetrical top molecule of point group C_{2v}. The three principle moments of inertia in order of increasing magnitude are designated I_A, I_B and I_C. Vibration–rotation bands are characterized as *A*, *B*, or *C* type depending on whether the dipole moment change is in the plane of the least, intermediate, or largest moment of inertia, respectively. According to Herzberg (*10*), the type of band determines the general character with respect to *P*, *Q*, and *R* branches and the ratio $\rho = I_A/I_B$ determines the relative position and intensities of the branches. The three moments of inertia for a bent M_1–M_2–M_1 molecule are

$$I_1 = 2M_1r^2 \sin^2\left(\frac{\theta}{2}\right) \tag{11}$$

$$I_3 = M_2r^2 \cos^2\left(\frac{\theta}{2}\right)\left[\frac{2M_1}{2M_1 + M_2}\right]^2 + 2M_1r^2 \cos^2\left(\frac{\theta}{2}\right)\left[\frac{2M_1 + M_2}{M_2}\right]^{-2} \tag{12}$$

$$I_2 = I_1 + I_3, \tag{13}$$

where M_1 is oxygen; M_2 is carbon; r, the C–O bond length; and θ, the OCO bond angle. The axis of I_1 is the C_2 axis of the molecule, the axis of I_2 is perpendicular to the plane of the molecule and the axis of I_3 is in the plane of the molecule perpendicular to the other two. To an approximation sufficient for this calculation, the spacing of successive rotational levels is inversely proportional to the moment of inertia of the axis of rotation. If the separation of the two branches of each envelope is proportional to the separation of the individual rotational levels, then

$$\frac{658.3 - 629.3}{647.2 - 630.9} = \frac{I_2}{I_1} = \frac{I_3}{I_1} + 1. \tag{14}$$

Substituting the values of 16 for M_1 and 12 for M_2,

$$\frac{29.0}{16.3} = \frac{3}{11}\cot^2\frac{\theta}{2} + 1; \theta \approx 60°. \tag{15}$$

Substituting in Eqs. (11) and (12) gives $I_1 = 8r^2$ and $I_3 = 6.54r^2$. The moments of inertia are $I_3 = I_A$; $I_1 = I_B$; and $I_2 = I_C$. Therefore the alternating dipole moment for the ν_1 vibration lies in the I_B axis, the axis of intermediate moment of inertia. Thus these are both type *B* bands. Herzberg (*10*), indicates that, for type *B* bands, no *Q* lines occur near the center but overlap the *P* and *R* branches. The structure indicated for type *B* bands with $\rho = 0.8$ is consistent with these bands reported for CO_2 on NaCl.

There was no band reported in the vicinity of 1278 cm^{-1}, the frequency calculated for $\nu_1CO_2^{16.90}$. The band at 2288 cm^{-1} indicates that some of the chemisorbed CO_2 intermedions are equivalent to CO_2 molecules that have accepted 0.90 electrons. It is likely that the intensity of the ν_1 vibration is related to the amount of deformation from the linear configuration. The addition of 0.90 electrons may not cause a sufficient decrease in the bond angle from 180° to make this absorption band strong enough to be detected. Walsh (*7*) indicates that the decrease in the internuclear angle from 17 to 18 electrons should be much greater than from 16 to 17 electrons.

In conclusion, these interpretations of some of the infrared bands attributed to adsorbed CO_2 suggest that

1. CO_2 intermedions may be polarized so strongly that their vibrational frequency corresponds to the acceptance of 1.90 electrons.
2. This polarization changes the structure of the molecule from linear to bent at a 60° angle.
3. Yet these CO_2 intermedions are so weakly bonded to the surface that they appear to be *rotating!* Rotations seems to exclude electron sharing and any type of covalent bonding.

The discovery of chemisorbed CO_2 intermedions has provided polarization fractions of 0.32 for zinc and 0.90 for sodium. It has indicated that the chemisorbed intermedions not only attain the vibrational frequency equivalent to the change in number of electrons but also the physical structure equivalent to this change.

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