VIBRATIONAL DYNAMICS OF ADSORBED CO_2: SEPARABILITY OF THE CO_2 ASYMMETRIC STRETCHING MODE

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Separability of the CO_2 asymmetric stretching mode is probed theoretically by performing highly accurate vibrational calculations on the CO_2 and K^+CO_2 model systems. The proposed approach is applied to a model case of the vibrational dynamics of the CO_2 molecule adsorbed in K-FER zeolite. The CCSD(T) level is fully adequate for quantitative decription of the CO_2 vibrational dynamics, and all important effects on the vibrational dynamics of CO_2 adsorption complexes can be estimated rather accurately (within 5 cm^{-1}) at the DFT level of theory.

Keywords: Adsorption of CO_2; Vibrational dynamics; DFT calculations; Adiabatic separation; *Ab initio* calculations; Adsorption; Vibrational spectroscopy.

Porous materials (e.g., metal-organic frameworks, porous carbons and crystalline aluminosilicates) represent a promising alternative to the liquid amine-based chemical solvents presently used on an industrial scale to stabilize and reduce atmospheric concentrations of greenhouse gases (GHGs)[1,2]. In particular, reversible adsorption of carbon dioxide in microporous solids such as alkali metal exchanged zeolites with well defined crystal stucture, has attracted a lot of research interest[3–10]. Systematic studies aimed at deeper understanding of gas-solid interactions often rely on combined spectroscopic and theoretical investigations. It has been demonstrated previously that the IR spectra of simple "probe" molecules along with precise quantum-chemical calculations can provide valuable insight

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into properties of adsorption sites[11,12]. Quite a few studies have focused on the vibrational dynamics of carbon monoxide adsorbed on protonic and alkali metal exchanged zeolites[14–16]. From a combination of experimental variable pressure IR spectra and the theoretical prediction of individual spectral features, detailed information about the coordination, localization, and distribution of extra-framework metal cations has been obtained[14]. Theoretical calculation of the spectroscopic signature of the adsorption complexes are typically carried out within the framework of the harmonic approximation. Thus, confrontation with experiment is done under the assumption of constant anharmonicity for free and adsorbed molecules. While this assumption clearly holds in some cases (e.g. for a CO molecule, see refs[11,13]), for polyatomic molecules it should be carefully examined.

To describe the vibrational dynamics of polyatomic molecules within the Born–Oppenheimer approximation it is suitable to rely on curvilinear valence coordinates (bond lengths and bond angles), as they allow construction of well-represented and mass-independent potential energy surfaces through the use of harmonic and other simple functional representations[17]. This advantage, however, is achieved at the expense of complicating the kinetic energy operator, which is intrinsically anharmonic in the curvilinear coordinates[17,18]. Consequently, the use of curvilinear coordinates is plagued by a very strong increase of the formal complexity of the theory with growth in the number of the vibrational degrees of freedom, and is thus limited to the case of small molecular systems.

For larger systems, one traditionally relies on rectilinear normal coordinates which provide the simplest representation of the molecular kinetic energy operators[19,20]. However, while ideal for constructing molecular kinetic energy operators, normal coordinates (defined as linear combinations of the tangential displacements of molecular atoms from their equilibrium configurations) are not the best choice for reflecting the actual shapes of the global potential energy surfaces. One way of overcoming this problem may consist of replacing the normal coordinates by their rectilinear analogues, which are optimized to resemble their curvilinear valence counterparts[21], or alternatively, to "invert" this procedure by constructing the appropriate curvilinear normal-mode-behaving vibrational displacements[22].

The principal problem faced in the actual implementations of these approaches arises due to the strong nonlinearity of the formulas defining the curvilinear coordinates in terms of their rectilinear counterparts and the finiteness of the convergence radii of the Plíva nonlinear (power series) transformations of the valence-force displacement coordinates to the cartesian displacement coordinates[23–25]. Fortunately, at least in principle, the

latter problems can be handled by replacing the approximate polynomial expansions by exact solutions of the transformation equations. Obviously, finding closed-form solutions for given problems is restricted to a very limited set of small and symmetric systems (see e.g. ref.[26]), and the only practical approach will thus be numerical. However, the resulting numerical results can easily be smoothed using suitable functional forms, and the approach thus made practical even in the case of large molecular systems. This approach appears to be especially promising in the case of molecular complexes involving very small and highly symmetric chromophores which are only weakly coupled to the rest of the probed systems. In such cases, the vibrational degrees of freedom of the chromophore can be separated, fairly accurately, from the remaining molecular degrees of freedom, and these in turn treated perturbatively (see e.g. ref.[27]). Consequently, the small chromophores can be treated "exactly", and thus serve as well defined spectral probes. To test this premise and to get deeper insight, we have found it worthwhile to probe it by means of model calculations. Specifically, we apply it to the case of the vibrational dynamics of a CO_2 molecule adsorbed in K-FER with the aim of resolving the disharmony between the standard normal coordinate analysis and standard DFT calculation theory and IR experiments[9,10].

METHODS

The linear XYZW molecular model. The definition of the vibrational valence-force and cartesian displacement coordinates of the studied complexes are given in Fig. 1. The bond-stretching coordinates, R_{XY}, R_{YZ} and R_{ZW}, are defined as the instantaneous displacements of the internuclear distances X–Y, Y–Z and Z–W (d^e_{XY}, d^e_{YZ} and d^e_{ZW} being their equilibrium values), and the angle-deformation coordinates, γ and χ, represent the instantaneous deviations of the valence angles, X–Y–Z and Y–Z–W, from linearity. Their orientations in space are defined by the projections, γ_x, γ_y and χ_x, χ_y of the coordinates γ and χ, respectively, in the *xz*- and *yz*- planes of the cartesian coordinate system.

$$d^e_{AB} + R_{AB} = \{(\delta x_B - \delta x_A)^2 + (\delta y_B - \delta y_A)^2 + (z^e_B - z^e_A + \delta z_B - \delta z_A)^2\}^{1/2} \qquad (1)$$

$$(d^e_{AB} + R_{AB})(d^e_{BC} + R_{BC})\cos(\pi + \beta) =$$

$$= (z_A^e - z_B^e + \delta z_A - \delta z_B)(z_C^e - z_B^e + \delta z_C - \delta z_B) +$$

$$+ (\delta x_A - \delta x_B)(\delta x_C - \delta x_B) + (\delta y_A - \delta y_B)(\delta y_C - \delta y_B) \qquad (2)$$

$$\tan\beta_x = \frac{(\delta x_A - \delta x_B)(z_C^e - z_B^e + \delta z_C - \delta z_B) + (\delta x_C - \delta x_B)(z_B^e - z_A^e + \delta z_B - \delta z_A)}{(z_B^e - z_A^e + \delta z_B - \delta z_A)(z_C^e - z_B^e + \delta z_C - \delta z_B) - (\delta x_A - \delta x_B)(\delta x_C - \delta x_B)} \qquad (3)$$

and

$$\tan\beta_y = \frac{(\delta y_A - \delta y_B)(z_C^e - z_B^e + \delta z_C - \delta z_B) + (\delta y_C - \delta y_B)(z_B^e - z_A^e + \delta z_B - \delta z_A)}{(z_B^e - z_A^e + \delta z_B - \delta z_A)(z_C^e - z_B^e + \delta z_C - \delta z_B) - (\delta y_A - \delta y_B)(\delta y_C - \delta y_B)} \qquad (4)$$

where A, B, and C are labels of the appropriate atoms (X, Y, Z and W) and $R_{AB} = R_{XY}$, R_{YZ} and R_{ZW}, and $\beta = \gamma$ and χ.

Assuming the vibrational displacements $\delta\alpha_A$ ($\alpha = x$, y and z; A = X, Y, Z and W) to be infinitesimal, we may approximate the above relations as power series in these displacements, and on retaining only terms which are linear in them, we obtain relations defining the so-called linearized valence-force coordinates R_{XY}^o, R_{YZ}^o, R_{ZW}^o, γ_x^o, γ_y^o, χ_x^o and χ_y^o as the following linearly independent combinations of the cartesian displacement coordinates

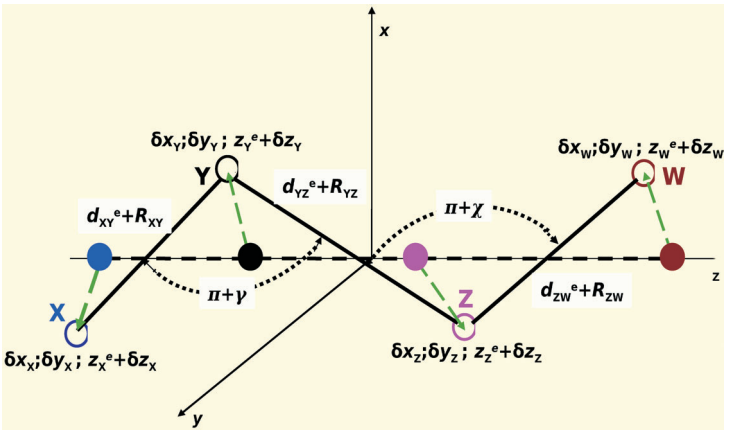

FIG. 1
Geometry of the linear XYZW molecule in equilibrium and in an arbitrary displaced configuration

$$R^o_{XY} = \delta z_Y - \delta z_X\,, \quad R^o_{YZ} = \delta z_Z - \delta z_Y\,, \quad R^o_{ZW} = \delta z_W - \delta z_Z$$

$$\gamma^o_x = (1/d^e_{XY})(\delta x_X - \delta x_Y) + (1/d^e_{YZ})(\delta x_Z - \delta x_Y)$$

$$\gamma^o_y = (1/d^e_{XY})(\delta y_X - \delta y_Y) + (1/d^e_{YZ})(\delta y_Z - \delta y_Y)$$

$$\chi^o_x = (1/d^e_{YZ})(\delta x_Y - \delta x_Z) + (1/d^e_{ZW})(\delta x_W - \delta x_Z)$$

$$\chi^o_y = (1/d^e_{YZ})(\delta y_Y - \delta y_Z) + (1/d^e_{ZW})(\delta y_W - \delta y_Z) \qquad (5)$$

The latter set of equations can be extended by adopting the usual mass-dependent Eckart conditions[17] (m_A being the mass of the atom A and $\mathbf{r}_A{}^e$ and $\mathbf{r}_A$ its equilibrium and actual position vectors, respectively)

$$\sum_A m_A \mathbf{r}_A = 0$$

$$\sum_A m_A \mathbf{r}^e_A \times \dot{\mathbf{r}}_A = \mathbf{0} \qquad (6)$$

and the extended system may be solved for the cartesian displacement coordinates. The resulting solutions can then be substituted into the definitions for the curvilinear coordinates, thus yielding exact relations between the curvilinear and linearized valence-force coordinates, and consequently the possibility to construct the vibrational Hamiltonian **H** in terms of the linearized coordinates. The corresponding mathematical manipulations are fairly straightforward, and it can easily be shown that

$$\mathbf{H} = \frac{1}{2} \sum_{k,l \in \Phi} G_{kl} P_k P_l + V(\mathbf{\Phi}) \qquad (7)$$

where $\mathbf{\Phi} \equiv \{\Phi_1, \Phi_2, \Phi_3, \Phi_{4a}, \Phi_{5a}, \Phi_{4b}, \Phi_{5b}\} = \{R^o_{XY}, R^o_{YZ}, R^o_{ZW}, \gamma^o_x, \gamma^o_y, \chi^o_x, \chi^o_y\}$, $P_m = -i\hbar\,\partial/\partial m$ ($m \in \mathbf{\Phi}$) and G_{kl} are elements of the symmetric Wilson matrix which factorises into one three-by-three block of symmetry Σ^+ with the following non-zero elements

$$G_{11} = (m_X + m_Y)/(m_X m_Y), \quad G_{22} = (m_Y + m_Z)/(m_Y m_Z)$$

$$G_{33} = (m_Z + m_W)/(m_Z m_W), \quad G_{12} = -1/m_Y\,, \quad G_{23} = -1/m_Z \qquad (8)$$

and two equivalent two-by-two blocks of symmetry Π defined by the following expressions ($G_{nama} = G_{nbmb}$; n, m = 4, 5)

$$G_{4a4a} = (d^e_{XY})^{-2} / m_X + (1/d^e_{XY} + 1/d^e_{YZ})^2 / m_Y + (d^e_{XY})^{-2} / m_Z$$

$$G_{4a5a} = -(d^e_{YZ})^{-1}(1/d^e_{XY} + 1/d^e_{YZ}) / m_Y - (d^e_{YZ})^{-1}(1/d^e_{YZ} + 1/d^e_{ZW}) / m_Z$$

$$G_{5a5a} = (d^e_{YZ})^{-2} / m_Y + (1/d^e_{YZ} + 1/d^e_{ZW})^2 / m_Z + (d^e_{ZW})^{-2} / m_W . \qquad (9)$$

For small vibrational displacements the linearized coordinates closely imitate the "genuine" curvilinear vibrational coordinates, thus giving evidence of their physical adequacy for dynamical calculations. Importantly, the kinematic coefficients G_{kl} of the pertinent Hamiltonian are constant, and the differences between the linearized and curvilinear coordinates are small enough to allow for their unambiguous evaluation and correct accounting. For larger vibrational displacements, however, use of the linearized coordinates may become questionable. Namely, for the displacements acquiring amplitudes with magnitudes that are comparable with the molecular equilibrium geometry characteristics, the defining Eqs (*1*)–(*4*) cannot be "inverted" unambiguously (see e.g. ref.[26]), and the linearized coordinates thus become ill-defined. One way of overcoming this problem consists of factorising the total molecular dynamical problem into two parts which solve the dynamics of the large-amplitude and small-amplitude motions separately. In principle, the separation can be achieved formally exactly by introducing an additional coordinate reference system which follows the large-amplitude motions and "moves", thus treating these motions from the vibrational problem into the associated rotational problem (see e.g. refs[28,29]).

In the case of systems consisting of weakly bound complexes, one can solve the problem by relying on the adiabatic separation of the vibrational degrees of freedom of fairly rigid molecular fragments (high-frequency motions) and of the complexation (low-frequency) motions (see e.g. ref.[30]). For instance, we may approximate the total vibrational wavefunction, Ψ_{tot}, as the following product

$$\Psi_{tot}(\mathbf{\Phi}) = \psi(\Phi_3, \Phi_{5a}, \Phi_{5b})\, \phi(\Phi_1, \Phi_2, \Phi_{4a}, \Phi_{4b}; \Phi_3, \Phi_{5a}, \Phi_{5b}) \qquad (10)$$

i.e., treat the low-frequency modes, Φ_3, Φ_{5a}, Φ_{5b}, as motions opposed by the effective potential which is generated by the remaining (high-frequency)

molecular motions. Equally well, the role of the low and high-frequency modes can be reversed, i.e., the total vibrational wavefunction can be expressed in its dynamically equivalent form where the low-frequency modes are treated as the dynamical variables and the high-frequency modes as the appropriate parameters. In any case, for this study the high-frequency modes corresponding to the small-amplitude motions can be treated using linearized coordinates.

The linear O–C–O···X complexes. As it was suggested in the previous section, it is suitable to treat these complexes using the adiabatic separation of the low-frequency (X atom involving) motions from the high-frequency motions of the strongly bound O–C–O fragment. For instance, to get the required effective potential energy function, $U_{\text{eff}}(R_{OC}, R_{CO}, \gamma_x, \gamma_y,$ one first solves the following Schrödinger equation (for a suitable grid of values of the high-frequency coordinates)

$$\mathbf{H}_{\text{eff}}\, \psi(R_{OX}, \chi_x, \chi_y) = U_{\text{eff}}(R_{OC}, R_{CO}, \gamma_x, \gamma_y)\, \psi(R_{OX}, \chi_x, \chi_y). \qquad (11)$$

Relying on relations (*1*)–(*4*), the pointwise generated potential U_{eff} can be transformed exactly into its linearized representation, $U_{\text{eff}}(R^o_{OC}, R^o_{CO}, \gamma^o_x, \gamma^o_y)$, where the linearized coordinates are defined by the appropriate subset of the Eq. (*5*).

The resulting effective potential energy and kinetic energy expressions may be simplified further thanks to the mass symmetry of the O–C–O fragment. Namely, after replacing R_{OC} and R_{CO} by their symmetrised versions,

$$S_1 = (R^o_{OC} + R^o_{CO}) / \sqrt{2}$$
$$S_2 = (R^o_{OC} - R^o_{CO}) / \sqrt{2} \qquad (12)$$

the corresponding vibrational Hamiltonian (*7*) simplifies to yield the following form

$$\mathbf{H} = \frac{1}{2} \sum_{k \in \Gamma} G_{kk} P_k^2 + V(\mathbf{\Gamma}) \qquad (13)$$

where $\mathbf{\Gamma} \equiv \{\Phi_1, \Phi_2, \Phi_{4a}, \Phi_{4b}\} = \{S_1, S_2, \gamma^o_x, \gamma^o_y\}$, $P_m = -i\hbar\, \partial/\partial m$ ($m \in \Gamma$) and G_{kl} are matrix elements of the Wilson matrix, for which it holds ($G_{4b4b} = G_{4a4a}$)

$$G_{11} = 1 / m_O, \quad G_{22} = 1 / m_O + 2 / m_C ,$$

$$G_{4a4a} = (d^e_{OC})^{-2} / m_O + (1/ d^e_{OC} + 1/ d^e_{CO})^2 / m_C + (d^e_{CO})^{-2} / m_O . \qquad (14)$$

To complete a theoretical rationalization of the vibrational dynamics of the probed fragment, i.e., to get the eigenvalues and eigenvectors of the Hamiltonian (*13*), it is fairly natural to diagonalize this Hamiltonian as a matrix in terms of basis sets which consist of eigenfunctions obtained numerically from the corresponding uncoupled one-dimensional Schrödinger equations for the stretching motions along the S_1 and S_2 coordinates, and analytic wavefunctions pertaining to the two-dimensional isotropic harmonic oscillator for the bending motions (γ^o_x, γ^o_y).

Ab initio calculations. The adiabatic potential energy functions of CO_2 and CO_2K^+ were evaluated (point-wise) on a geometry grid involving a wide range of values of the valence-force curvilinear coordinates. The calculations for CO_2 were performed at the coupled cluster level, explicitly accounting for single and double excitations and perturbative triple excitations, at the CCSD(T) and at the DFT levels employing PBE exchange correlation functional[32]. The potential energy surface for CO_2K^+ (2040 grid points) was calculated at the PBE level only. The Dunning correlation-consistent cc-pVQZ basis set and combinations of CVQZ and cc-pVQZ basis sets were used for CO_2 and CO_2K^+, respectively[33,34]. Calculations were performed with the Molpro 09 and Gaussian 03 program suits[35,36].

RESULTS AND DISCUSSION

The point-wise defined energy data were smoothed by a power series expansion fit in terms of the curvilinear coordinates defined by Eqs (*1*)–(*4*). The original "curvilinear" geometry grids were transformed into their linearized counterparts by inverting definitions (*1*)–(*4*) with respect to the linearized coordinates defined by Eq. (*5*), and in turn the corresponding "linearized" representations of the processed potential energy functions were determined by the same kind of fitting as in the case of their "curvilinear" representations. Interestingly, while we had no problem performing these calculations for OCO, for $OCOK^+$ the procedure failed due to poor convergency of the power series. To resolve this problem, we decided to integrate over the low-frequency motions of the complex using the adiabatic approximation given by Eq. (*11*), and to probe the vibrational dynamics of OCO using the effective potentials $U_{\text{eff}}(R_{OC}, R_{CO}, \gamma_x, \gamma_y)$ provided by this ap-

proximation. To get insight on the effects of the low-frequency motions on the high-frequency motion of the OCO fragment and adequacy of the adopted approximation, the effective potentials U_{eff} were generated by solving the problem (*11*) while respecting anharmonicity of the low-frequency modes, on the one hand, and assuming them to be harmonic, on the other. We have also performed the scheduled dynamical calculations with complete neglect of these modes. Not surprisingly, just as in the case of the isolated OCO molecule, all the effective potentials were found to be quantitatively represented in terms of strongly converging power series, and are thus suitable for dynamical calculations.

The results of the reported calculations are illustrated by the Tables SM1 and SM2 of the attached Supplementary material, and by Tables I and II of the main part of this paper (note that the linearized coordinates S_1, S_2, γ_x and γ_y are *de facto* normal coordinates which can easily be scaled to their dimensionless representation, which allows for a straight assessment of their magnitudes). Table SM1 documents the fast convergency of the processed potentials and also the very high accuracy of the CCSD(T) method. A brief inspection of the table also illustrates the fairly reasonable accuracy of the DFT off-diagonal force constants, thus showing promising potential for combined ab initio calculations which would consist of a CCSD(T) evaluation of the diagonal force constants and a DFT evaluation of the off-diagonal constants. The purpose of Table SM2 is to show that the standard quartic expansion of the potential energy functions in the curvilinear coordinates is adequate not only for the rigid molecular fragment OCO, but also for its weakly bound complex $OCOK^+$.

TABLE I
Fundamental vibrational frequencies of isolated CO_2 (in cm^{-1})

Frequency	Empirical[a]	CCSD(T)[b]	PBE[b]
ν_1	1285.2	1282.4	1240.0
ν_2	666.6	665.5	639.1
ν_3	2349.3	2348.7	2312.9
$(\omega_3 - \nu_3)$[c]	47.2	47.8	45.9

[a] The values calculated (with neglecting the Coriolis contributions) from the potential energy function evaluated in ref.[31] by fitting to experiment; [b] present study; [c] ω labels harmonic frequencies.

The results in Table I further illustrate the accuracy of the CCSD(T) method, and more importantly, the good consistency between the CCSD(T) and DFT approaches. While DFT results are not quantitative, they provide reliable estimates for the frequency shifts arising due to anharmonic effects. This observation is rather important with respect to previous calculations on CO_2 adsorption complexes in various environments that were performed at the DFT level. In a previous study of vibrational dynamics of CO_2 in zeolite K-FER, good consistency between CCSD(T) and DFT has also been shown for the effects on ω_3 due to interactions with an extra-framework cation and with the zeolite framework oxygen atoms. Table II summarizes changes in CO_2 anharmonic frequencies in the $OCOK^+$ complex calculated with various dynamical models. The dynamical effects due to the low-frequency vibrational modes of the complex are rather negligible, and consequently a harmonic treatment of the low-frequency modes is fully adequate.

In summary, it has been clearly shown in Tables I and II that the effects on vibration dynamics of CO_2 due to adsorption in alkali-metal exchanged zeolites can be reliably described at the DFT level (using the PBE exchange-correlation functional) within the harmonic approximation. In light of this conclusion, the results obtained previously for CO_2 adsorption in K-FER zeolite can be reviewed. The results obtained for K^+CO_2 and recent computational results reported for FK CO_2 and FK $CO_2\cdots H_2O$ model systems and for CO_2/K-FER and CO_2/silicalite[9] are summarized in Table III. Based on the results reported in Tables I–III the following observation can be drawn: (i) Vibrational dynamics of free CO_2 obtained at the CCSD(T) level are in perfect agreement with experimental data. (ii) The anharmonicity of the

Table II
DFT fundamental vibrational frequencies of CO_2K^+ (in cm^{-1})

Frequency	Anharmonic[a]	Harmonic[b]	Frozen[c]
ν_1	1222.5	1222.0	1222.9
ν_2	627.7	627.4	629.4
ν_3	2331.0	2331.0	2332.1
$(\omega_3 - \nu_3)^c$	42.4	42.4	41.3

[a] Calculated with respecting anharmonicity of the low-frequency modes; [b] calculated with treating the low-frequency modes as harmonic; [c] calculated with fixing R_{OK} and χ_x and χ_y at their equilibrium values.

ν_3 mode ($\omega_3 - \nu_3$) in CO_2 obtained at both CCSD(T) and PBE levels of theory is in a very good agreement with the experimental value. (iii) The anharmonicity of the ν_3 mode in K^+CO_2 is only about 4 cm^{-1} smaller than that found for free CO_2; thus, the effects on vibrational dynamics of CO_2 adsorption complexes can be safely described within the harmonic approximation. (iv) The harmonic complexation shift decreases in the order K^+CO_2 > FK CO_2 > FK $CO_2\cdots H_2O$. (v) DFT correctly (quantitatively) describes the fact that the ν_3 frequency decreases upon the adsorption in silicalite. It is therefore reasonable to expect that DFT will describe quantitatively the effects on vibrational dynamics of CO_2 adsorbed in K-FER zeolite.

Two bands in the ν_3 stretching region are observed experimentally; the 2346 cm^{-1} band that is red-shifted by 3 cm^{-1} from the value found for free CO_2 has been assigned to CO_2 adsorption complexes on extra-framework K^+ cations in K-FER, and the 2355 cm^{-1} band (blue-shifted by 6 cm^{-1}) has been assigned to CO_2 adsorbed in between two extra-framework K^+ cations (a dual cation site)[9,10]. The results presented above make this assignment somewhat uncertain. In particular, the calculated $\Delta\omega_3$ shift for CO_2 adsorbed on a single extra-framework K^+ cation (+10 cm^{-1}) is in good agreement with the +6 cm^{-1} shift observed for the 2355 cm^{-1} band. It is apparent from Table III that PBE calculations give $\Delta\omega_3$ shifts in good agreement with CCSD(T) or experiment (whatever is available); it is reasonable to assume also that for CO_2 adsorption in K-FER the PBE shifts should be correct. Note that the experimental IR spectra of CO_2/K-FER show just standard dependence on temperature (bands are blue-shifted by about 2 cm^{-1} going from 300 to 100 K). As it has been noted above, the assignment of

TABLE III
Harmonic complexation shifts, $\Delta\omega_3$, for CO_2 in various environment (in cm^{-1})

System	PBE[b]	CCSD(T)[b]	Experiment[c]
K^+CO_2	14.6[a]	14.6	
FK CO_2	5.0	6.7	
FK $CO_2\cdots H_2O$	2.3	4.1	
CO_2/K-FER	~10		–3, 6
CO_2/Silicalite	–6, –9		–8

[a] Present work; [b] ref.[9]; [c] refs[9,10]

2355 and 2346 cm^{-1} bands proposed in refs[9,10] is somewhat doubtful. However, that assignment is consistent with the conclusions reached for similar systems (CO_2 and CO adsorption in various alkali-metal exchanged zeolites). To fully dismiss this assignment it is necessary to assign a band at 2346 cm^{-1} as well. At present we do not have any reasonable interpretation for this band if we assume that CO_2 adsorption complexes on single K^+ sites correspond to the 2355 cm^{-1} band.

CONCLUSIONS

A general theory for anharmonic treatment of vibrational dynamics of CO_2 interacting with M^+ adsorption sites in microporous solids has been developed. The approach based on the adiabatic separation of the low-frequency motions from the high-frequency motions of the interacting O–C–O fragment has been applied to the model case of the vibrational dynamics of a CO_2 molecule adsorbed in K-FER zeolite. The main results of this study can be generalized as follows: (i) The CCSD(T)/cc-pVQZ level is fully adequate for quantitative decription of CO_2 vibrational dynamics and (ii) all important effects on the vibrational dynamics of CO_2 adsorption complexes can be rather accurately (within 5 cm^{-1}) estimated at the DFT level of theory. These conclusions not only justify previous DFT studies on reversible adsorption of CO_2 in alkali metal exchanged zeolites, but can also serve as a basis for future development of molecular dynamics models of adsorption processes. Such models are obviously necessary to explain a rather intricate balance between polarization effects due to M^+ cations (blue-shifting the ν_3 band of CO_2) and interactions with the framework oxygens (red-shift).

Quite generally, the proposed adiabatic separation of the vibrational motions can be reversed by averaging over the high-frequency modes and explicitly treating only their low-frequency counterparts. However, mostly due to profound anharmonicities of the low-frequency motions, the rectilinear coordinate description may not be suitable and should be replaced by a curvilinear approach[18] (possibly in a combination with a vibrational self-consistent field procedure[37,38], which may allow for an additional reduction of the treated vibrational degrees of freedom).

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