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Relation Between Bond Angle and Carbon−Oxygen Stretching Frequencies in CO_2−Containing Compounds

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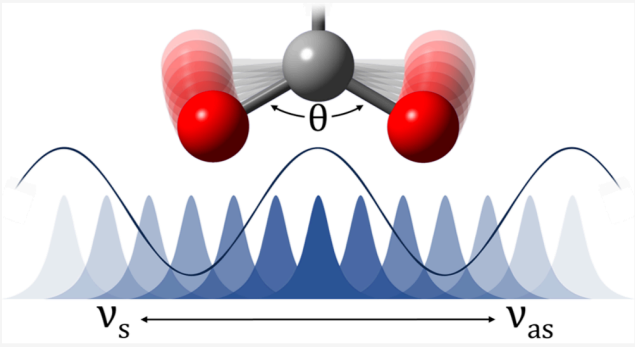
ABSTRACT: The symmetric (ν_s) and antisymmetric (ν_{as}) O−C−O stretching modes of CO_2-containing compounds encode structural information that can be difficult to decipher, due to the sensitivity of these spectral features to small shifts in charge distribution and structure, as well as the anharmonicities of these two vibrational modes. In this work, we discuss the relation between the frequency of these modes and the geometry of the O−C−O group, showing that the splitting between ν_s and ν_{as} ($\Delta\nu_{as\text{-}s} = \nu_{as} - \nu_s$) can be predicted based only on the O−C−O bond angle obtained from quantum chemical calculations with reasonable accuracy (± 46 cm^{-1}, $R^2 = 0.994$). The relationship is shown to hold for the infrared spectra of a variety of CO_2-containing molecules measured in vacuo. The origins of this model are discussed in the framework of elementary mode analysis.



INTRODUCTION

CO_2-containing compounds are abundant across a large array of chemical contexts. Carboxylates and carboxylato complexes, i.e., molecules of the form R−COO$^-$ and their salts, are ubiquitous in chemical reactions, commonly playing roles as nucleophiles, intermediates, or coordination ligands for metal ions.[1−3] Carboxylate functional groups often participate in the core functionality of a given molecule, e.g., as part of the binding pocket of a protein or by complexing the metal center of a catalyst.[4−8]

The vibrational signatures of the O−C−O groups, the symmetric (ν_s) and antisymmetric (ν_{as}) O−C−O stretching modes, are typically well-resolved and intense, and both modes are infrared active for carboxylates. In the case of the antisymmetric stretching mode, these peaks are typically in a region with low spectral congestion, making them easier to identify than many other features in the fingerprint region of the spectrum. The positions of the carboxylate stretching signatures are sensitive to subtle changes in complex structure and charge distribution, making them both challenging to interpret and desirable to model.[9−11] Here, we present a simple and generalizable relationship between the frequencies of the O−C−O stretching modes and the O−C−O bond angle (θ_{OCO}).

While quantum chemical calculations are highly useful for comparison between experimental and simulated infrared spectra in order to identify the most likely structure of a compound and assign infrared features, it is of fundamental interest to elucidate the structure−spectrum relationship of the individual carboxylate stretching modes. Moreover, identifying a simple relationship between the spectral and structural features of a carboxylate group makes for an easy and secure assignment of features in congested spectra, where even quantum chemical calculations may not allow unambiguous and simple recognition of spectral patterns for peak identification. The assignment of the antisymmetric stretching band is often straightforward since its intensity is usually rather high. However, the symmetric stretching mode is usually more difficult to distinguish from other modes in the same spectral region since it is weaker and often in a congested region of the spectrum. In fact, they are often mixed with other local oscillators. While the mode with the most intense peak in the region of the symmetric O−C−O stretching mode usually has the largest O−C−O stretching amplitude, a connection between the splitting of the modes and the local O−C−O bond angle would be of interest to help in assigning the spectral features.

A seemingly straightforward task, the search for an explicit correlation between the positions of the carboxylate bands and molecular geometry, has spanned decades. Deacon and Phillips wrote an extensive, foundational review in 1980 which relates the symmetric and antisymmetric O−C−O stretching frequencies of carboxylato complexes (specifically, the splitting between them, $\Delta\nu_{as\text{-}s}$) with the coordination motif of the carboxylate

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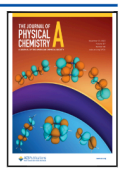

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group.[12] They classified carboxylates into unidentate, bidentate, bridging, and pseudobridging binding patterns and found a rough empirical relationship between binding motif and $\Delta\nu_{as\text{-}s}$. This work was instrumental in establishing the influence of carboxylate coordination geometry on spectral signatures, and specifically identified both the length difference between connected C−O bonds and the O−C−O bond angle as the likely drivers of shifts in the carboxylate spectral features.

However, the authors noted many exceptions to the reported trends, and further explained that their observations did not generalize to multicarboxylate systems, concluding their paper with the statement: "It is evident that factors affecting the separations between the carbon−oxygen stretching frequencies are more complex than differences between carbon−oxygen bond lengths or the size of the O−C−O angles alone." While this is pioneering work, their necessary reliance on solution-phase and crystallographic data introduced spectral effects not solely dependent on molecular structure, obscuring the very relationships they were examining.

Sixteen years later, in 1996, Nara and colleagues took up the mantle and performed an investigation based on *ab initio* molecular orbitals of coordinated carboxylate groups and their stretching frequencies.[13] They produced the following relationship between the structure and peak splitting, $\Delta\nu_{as\text{-}s}$, of the carboxylate groups (in cm^{-1}):

$$\Delta\tilde{\nu}_{as\text{-}s} = 1818.1\delta_r + 16.47(\theta_{OCO} - 120^\circ) + 66.8 \quad (1)$$

where δ_r is the difference between the two C−O bond lengths (in Å) and θ_{OCO} is the O−C−O bond angle (in degrees). This result proposes a functional form for the two key structural influences on the carboxylate stretches highlighted by Deacon and Phillips, the C−O bond lengths and the O−C−O angle. However, they employed a harmonic treatment of these modes over a limited range of O−C−O angles, which led them to linearize the more complicated relationship between $\Delta\nu_{as\text{-}s}$ and θ_{OCO}. Similar to a linear approximation in a Taylor series, this treatment does not yield a trigonometric behavior in θ_{OCO}, specifically for a bond angle approaching 180°, and in addition, the harmonic approximation results are incompatible with experimental observations. Overall, the predictive power of the model is therefore severely limited.

The next major development in pursuit of an elegant correlation between structural parameters of O−C−O type compounds and their spectral signatures came from Brinzer and colleagues in 2015. They reported a two-dimensional infrared spectroscopic study of CO_2 dissolved in a variety of ionic liquids.[14] In discussing their results, they posited that the stretching modes of the CO_2 molecules they observed could be described with a simple model of the vibrational Hamiltonian constructed in a vibrational local-mode basis:

$$\underline{\boldsymbol{H}} = \begin{pmatrix} \hbar\omega_1 & \beta \\ \beta & \hbar\omega_2 \end{pmatrix} \quad (2)$$

where ω_i $(i = 1, 2)$ is the local mode frequency of C−O oscillator i, and β is the coupling between the two local modes. Extracting the eigenvalues of this matrix produces the symmetric and antisymmetric O−C−O stretching modes. The frequencies of these modes depend on the individual oscillator energies $(\hbar\omega_i)$, which are related to the individual C−O bond lengths, and the coupling constant between the two local modes (β) which is a function of the O−C−O bond angle. The authors then applied a linear fit to both of these parameters, generating equations that reproduced their experimental values quite well. This model is not generalizable to compounds with significantly more acute O−C−O angles, owing to the limited data set they are based on which consists of CO_2 molecules that remain largely linear across different solvent environments. This linearity not only prevents sampling the relationship between the positions of the CO_2 stretches and the O−C−O bond angle through a wide range of values, but also renders the symmetric stretch effectively infrared inactive, preventing a more rigorous experimental benchmarking of this model. However, their local-mode approach to dissecting individual contributions to the carboxylate stretching energies is important, as it provides a physical picture for the connection between the O−C−O stretching modes and molecular geometry.

In this work, we describe the relation between the O−C−O bond angle and the splitting between positions of the symmetric and antisymmetric O−C−O stretches. The model presented here is quantitative, has concrete physical origins, is generalizable to a multitude of systems and successfully describes a very large part of the existing data.

THEORETICAL APPROACH

The local-mode approach used by Brinzer et al. describes the coupling of two local C−O oscillators to produce two molecular normal modes: the symmetric and antisymmetric stretches.[14] We begin with an analogous ansatz for the vibrational Hamiltonian:

$$\underline{\boldsymbol{H}} = h\begin{pmatrix} \nu_1 & \alpha \\ \alpha & \nu_2 \end{pmatrix} \quad (3)$$

Here, $h\nu_1$ and $h\nu_2$ are the energies of the two individual C−O oscillators, and $h\alpha$ represents the coupling between the two oscillators. Diagonalizing the Hamiltonian yields an expression for the normal mode energies, which can be expressed in the frequencies of the symmetric and antisymmetric stretching modes:

$$\nu_{as,s} = \bar{\nu}_{1,2} \pm \frac{1}{2}\sqrt{4\alpha^2 + \Delta\nu_{1,2}{}^2} \quad (4)$$

In this description, $\bar{\nu}_{1,2}$ is the average of the two local oscillator frequencies, $\Delta\nu_{1,2}$ is their difference, and the antisymmetric and symmetric stretching modes result from the addition or subtraction of the second term, respectively. In the case of a symmetric O−C−O group, i.e., if the C−O bond lengths are equal and thereby the corresponding force constants and anharmonicities can be assumed to be the same, $\Delta\nu_{1,2}$ becomes 0.[15,16] In this regime, the expression for the splitting between the antisymmetric and the symmetric modes can be reduced to

$$\Delta\nu_{as\text{-}s} = \nu_{as} - \nu_s = 2\left(\frac{1}{2}\sqrt{4\alpha^2 + \Delta\nu_{1,2}{}^2}\right) = 2\alpha \quad (5)$$

resulting in a simple dependence on the coupling parameter (α). In the case of $\alpha = 0$, the uncoupled C−O components would oscillate independently. It has long been realized that the coupling between oscillators in CO_2-containing compounds is related to the O−C−O bond angle.[11,12,17] Although the exact relation is certainly more complex, we find that α can be expressed as a function of only θ_{OCO} with a remarkable degree of accuracy (discussed below). To quote Badger's remarks on his observation of the empirical relationship between the equilibrium bond length (r_e) and the force constant of the associated oscillator, "The fact that such a simple relation can be

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found is apparently due to the fact that the several factors on which r_e depends do not vary in an arbitrary and independent fashion through a set of molecules, but change in a more or less parallel manner."[15] In the present case, the many factors influencing α seem to vary together as well, allowing θ_{OCO} to serve as a descriptive parameter of the system as a whole.

RESULTS AND DISCUSSION

Experimentally determined values of $\Delta\nu_{as\text{-}s}$ were extracted from a series of gas-phase vibrational spectra of symmetric CO_2-containing compounds (see Supporting Information for data set used in fit).[18−28] By plotting the observed values of $\Delta\nu_{as\text{-}s}$ against the calculated O−C−O bond angle, as shown in Figure 1, we can extract an empirical relationship between the mode coupling constant α and θ_{OCO}.

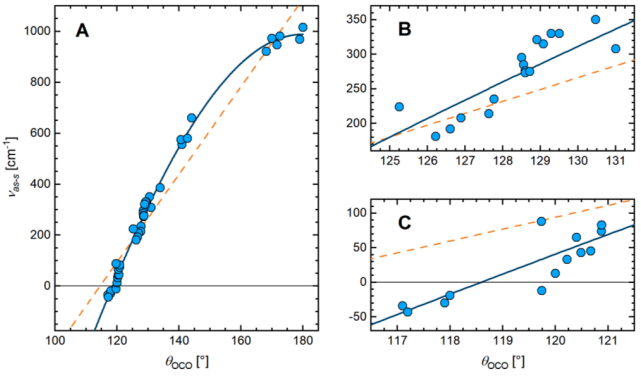

Figure 1. Relationship of $\Delta\nu_{as\text{-}s}$ and θ_{OCO}. Blue circles represent experimental $\Delta\nu_{as\text{-}s}$ values of CO_2-containing compounds included in the fit, the full line is a cosine fit function (see text) up to $\theta_{OCO} = 180°$, and the dashed orange line is a linear fit to the same data points. (A) Experimental data and the cosine fit function. (B) Enlarged view of the cluster of points near $\theta_{OCO} = 130°$. (C) Enlarged view of points with $\Delta\nu_{as\text{-}s} < 0$.

Visually, the correlation between $\Delta\nu_{as\text{-}s}$ and θ_{OCO} suggests a trigonometric function that crosses the θ-axis just before 120° and reaches its maximum near 180°. Fitting with a cosine (eq 6) produces an excellent match to the data and yields an R^2 value of 0.994, with residuals below 46 cm^{-1}. The seemingly trigonometric behavior of $\Delta\nu_{as\text{-}s}$ implies that the splitting is maximized when the O−C−O group approaches linearity ($\theta_{OCO} = 180°$) and minimized with a bent geometry ($\theta_{OCO} \approx 120°$). The splitting between the symmetric and antisymmetric stretching modes in cm^{-1} is well-described by eq 6.

$$\Delta\nu_{as\text{-}s} = 2\alpha = -(907.0\ \text{cm}^{-1} + 1895.5\ \text{cm}^{-1}\cos(\theta_{OCO})) \tag{6}$$

As θ_{OCO} varies, so too does the coupling constant (α) and, in turn, $\Delta\nu_{as\text{-}s}$. At ca. 120°, α approaches zero, so the uncoupled C−O bonds independently oscillate near their native frequencies (eq 5). The opening of the bond angle toward 180° brings about stronger interaction between the C−O local modes through the increasing coupling parameter and, therefore, concomitant growth in the symmetric-antisymmetric peak splitting. In passing, we note that an overall linear fit to the data (see Figure 1) performs poorly. A linear fit limited to the range $116° \le \theta_{OCO} \le 144°$ (representing a Taylor series expansion to the linear term around 130°) does not produce a more accurate prediction of $\Delta\nu_{as\text{-}s}$ than eq 6.

The functional form of this relationship is consistent with normal-mode analysis following Wilson's FG method.[17] This approach encodes the potential energy through the force constants of the molecule in terms of a given set of internal coordinates in a matrix $\underline{\boldsymbol{F}}$. It expresses the kinetic energy through a matrix $\underline{\boldsymbol{G}}$, which represents the motion of the atoms in the same internal coordinates and has dimensions of an inverse mass. We represent the O−C−O group using a general model for a nonlinear triatomic. This model neglects the "R" of an R−COO$^-$ molecule, and we further simplify it by limiting our treatment to the CO stretching coordinates, resulting in the $\underline{\boldsymbol{F}}$ and $\underline{\boldsymbol{G}}$ being 2 × 2 matrices.

$$\underline{\boldsymbol{F}} = \begin{bmatrix} F_r & F'_{rr} \\ F'_{rr} & F_r \end{bmatrix};\ \underline{\boldsymbol{G}} = \begin{bmatrix} G_r & G'_{rr} \\ G'_{rr} & G_r \end{bmatrix} \tag{7}$$

Multiplying them, we obtain the following matrix:

$$\underline{\boldsymbol{FG}} = \begin{bmatrix} F_rG_r + F'_{rr}G'_{rr} & F_rG'_{rr} + F'_{rr}G_r \\ F'_{rr}G_r + F_rG'_{rr} & F'_{rr}G'_{rr} + F_rG_r \end{bmatrix} \tag{8}$$

Obtaining the eigenvalues of this matrix produces the eigenvalues $\lambda_\pm$

$$\lambda_\pm = F_rG_r + F'_{rr}G'_{rr} \mp (F'_{rr}G_r + F_rG'_{rr}) \tag{9}$$

which are proportional to the squares of the normal mode energies, as given by

$$\lambda_+ = 4\pi^2c^2\nu_{as}^2;\ \lambda_- = 4\pi^2c^2\nu_s^2 \tag{10}$$

where c is the speed of light. Using these two expressions, the splitting between normal modes can be presented in terms of $\underline{\boldsymbol{FG}}$ matrix elements. First, eq 9 provides the difference between eigenvalues,

$$\Delta\lambda_\pm = \lambda_+ - \lambda_- = -2(F'_{rr}G_r + F_rG'_{rr}) \tag{11}$$

and the difference between normal modes ($\Delta\nu_{as\text{-}s}$) can be extracted from eq 10:

$$\Delta\lambda_\pm = \lambda_+ - \lambda_- = 4\pi^2c^2(\nu_{as}^2 - \nu_s^2) \tag{12}$$

$$= 4\pi^2c^2(\nu_{as} - \nu_s)(\nu_{as} + \nu_s) \tag{13}$$

$$= 4\pi^2c^2(\Delta\nu_{s\text{-}as})(2\overline{\nu}_{s,as}) \tag{14}$$

Combining eqs 11 and 14 and then isolating $\Delta\nu_{as\text{-}s}$ gives an expression for the splitting between the symmetric and antisymmetric stretches, as determined by normal-mode analysis:

$$4\pi^2c^2(\Delta\nu_{s\text{-}as})(2\overline{\nu}_{s,as}) = -2(F'_{rr}G_r + F_rG'_{rr}) \tag{15}$$

$$\Delta\nu_{s\text{-}as} = -\frac{1}{4\pi^2c^2\overline{\nu}_{s,as}}(F'_{rr}G_r + F_rG'_{rr}) \tag{16}$$

where $\overline{\nu}_{s,as}$ is the average of the symmetric and antisymmetric O−C−O stretching frequencies.

Calculated $\underline{\boldsymbol{G}}$ matrix values are given in ref 17,

$$G_r = \mu_C + \mu_O;\ G'_{rr} = \mu_C\cdot\cos\theta \tag{17}$$

where μ_x is the reciprocal mass of atom x. It is of note that while μ_O is constant for all of the systems discussed in this paper, the effect that μ_C has on the rest of the complex will vary with different carbon substituent groups, and we consider it an effective reciprocal mass. Substitution of these $\underline{\boldsymbol{G}}$ matrix values

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into eq 16 yields an equation for the energy splitting between normal modes in terms of physical parameters:

$$(\Delta\nu_{s\text{-}as}) = -\frac{1}{4\pi^2 c^2 \overline{\nu}_{s,as}}(F'_{rr}(\mu_C + \mu_O) + F_r(\mu_C \cdot \cos\theta)) \quad (18)$$

Note that this expression has the same functional form for the angular dependence of the splitting, as was found in the empirical fit shown above (eq 6):

$$(\Delta\nu_{s\text{-}as}) = -A(B + C\cdot\cos\theta) \quad (19)$$

Setting eq 6 equal to eq 18 thus allows the empirical relationship between $\Delta\nu_{s\text{-}as}$ and the bond angle to be evaluated in the framework of normal-mode analysis. To this end, eq 18 contains four possible variables to parametrize: μ_C (effective reciprocal mass of the C atom), $\overline{\nu}_{s,as}$ (average energy of the two normal modes), F_r (diagonal $\underline{F}$ elements representing the force constant for one local mode), and F_{rr}' (off-diagonal $\underline{F}$ elements representing the force constant between both local modes). We judge that μ_C is best approximated as the reciprocal mass of C and therefore held constant, given that there is not a straightforward way to determine how μ_C should vary for the different systems discussed here. The average normal mode energy, $\overline{\nu}_{s,as}$, also differs across complexes. Attempts to functionalize $\overline{\nu}_{s,as}$ in terms of bond angle were unsuccessful and produced an overall worse fit to the data when they were included in the complete expression. A simple solution then is to use the mean value of the systems included here, 1526 cm^{-1}, and we judge that for the purpose of the present work, a simple empirical relationship that captures most of the relevant physics is preferable over a possibly more accurate but also more complicated description.

Employing these approximations, F_r and $F_{rr'}$ can be extracted as 20.4 and 5.6 mdyne/Å, respectively. For comparison, ref 17 reports the value of the stretching force constant (F_r) as 11.8−13.4 mdyne/Å for a C═O bond and 5−5.8 mdyne/Å for a C−O bond. Additional physical insight can be gained by using the measured values of ν_s and ν_{as} to calculate F_r and $F_{rr'}$ for each complex, the expressions for which are acquired by rearrangement of eq 11:

$$F_r = \frac{2\pi^2 c^2}{(G'^2_{rr} - G_r^2)}(\nu_{as}^2(G'_{rr} - G_r) - \nu_s^2(G'_{rr} + G_r)) \quad (21)$$

$$F_{rr}' = \frac{2\pi^2 c^2}{(G_r^2 - G'^2_{rr})}(\nu_{as}^2(G_r - G'_{rr}) - \nu_s^2(G_r + G'_{rr})) \quad (22)$$

Plotting the ratio between the force constants, $F_{rr'}/F_r$, against the O−C−O bond angle reveals that the off-diagonal elements become nearly as large as the diagonal ones as θ_{OCO} increases (Figure 2). This further substantiates the observation highlighted with the local-mode approach (eq 6) that the coupling between the two oscillators reaches its maximum value when θ_{OCO} approaches 180°. Additionally, the mean values for F_r and $F_{rr'}$ calculated in this manner are 13.1 and 7.5 mdyne/Å, in excellent agreement with the literature value of F_r for a C═O bond.[17]

Deviations from the curve predicted by eq 6 can then be attributed to three main factors: (i) differences in local C−O oscillator force constants, (ii) differences in the effective reciprocal mass of the carbon atom, and (iii) different quality of the fit in different regions of θ due to the sparseness of available data. The C−O bond strength varies throughout the complexes included in the empirical fit and is inversely proportional to the predicted splitting (eq 18). Additionally, both the mass of an R group and its interaction with the carbon atom contribute to the effective reciprocal mass of C, since the approximations made in treating R-COO^- as a simple triatomic molecule remove individual contributions of an R group from consideration. As μ_C increases, the splitting is predicted to decrease. Since the empirical fit does not account for these parameters, it corresponds to an average representation of the variations in effective μ_C and local oscillator energies, which appear to largely vary together. Additionally, the available data on carboxylate complexes that meet the inclusion criteria (gas phase, symmetric) are sparse in some regions of θ_{OCO}. Least-squares fitting favors areas with a higher density of data points, as minimizing the error in a more populous region of the fit will lower the overall error more than by optimizing sparser regions of the fit that contribute fewer residual values to the total.

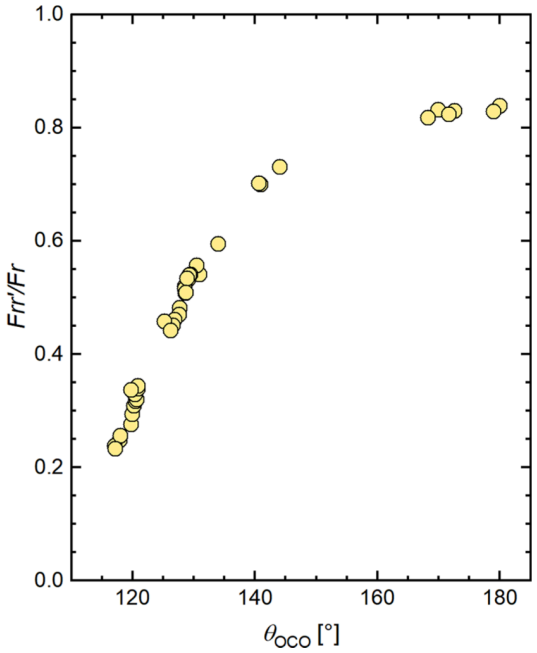

Figure 2. Ratio between diagonal and off-diagonal force constants vs the O−C−O bond angle for each complex included in the empirical fit (see Figure 1 and associated discussion).

Figure 3 demonstrates the comparison to selected data points from Deacon and Phillips's work, with the inclusion criteria being that the complex is monocarboxylic and that both the symmetric and antisymmetric stretching modes were reported (and that only one frequency was reported per mode) as well as the calculated O−C−O bond angle and C−O bond lengths.

The complexes with a larger difference between carboxylate C−O bond lengths deviate significantly from the predicted curve; the points with $\Delta\nu_{as\text{-}s}$ > 200 cm^{-1} have reported differences of more than 0.05 Å. Even though the data are crystallographic and many of the complexes are asymmetric, comparison of the empirical fit to experimental data from the original review by Deacon and Phillips yields a fairly good match.

■ CONCLUSIONS

In summary, we have presented a simple model that predicts the splitting between the symmetric and antisymmetric stretching frequencies of CO_2-containing compounds as a function of just

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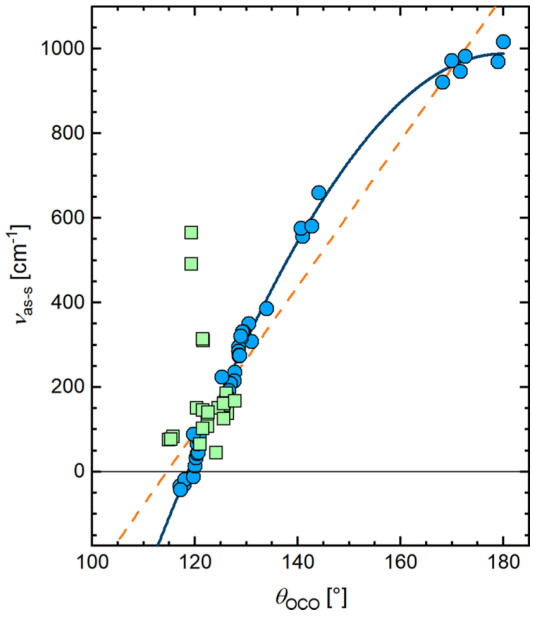

Figure 3. Green squares represent experimental data from Deacon and Phillips's review.[12] Blue circles represent experimental $\Delta\nu_{as\text{-}s}$ values of CO_2-containing compounds included in the fit and the full line is a cosine fit function (see Figure 1 and associated discussion).

the O−C−O bond angle (eq 6). This relation is based on a vibrational local-mode framework informed by several independent gas-phase measurements of CO_2 and R−COO^- type compounds. Through normal-mode analysis, the physical origins of the model are examined: O−C−O bond angle, C−O bond lengths, and effective mass of the R−C unit. These structural parameters appear to vary in tandem with one another, permitting the simplicity of our proposed model. The relation put forth here generalizes to a multitude of molecules, and we anticipate that it may be used to further predict or interpret experimental spectra of CO_2-containing compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.3c05082.

Methods, experimental values used for empirical fit, geometry calculation information, and selected data from the Deacon and Phillips review (ref 12) (PDF)

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Notes

The authors declare no competing financial interest.

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