

On the Electronic Coupling of the C=O Stretching Vibrations in $\text{Cl}_2\text{Pt}(\text{malonate})^-$

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Ab initio calculations on the complex $\text{Cl}_2\text{Pt}(\text{malonate})^-$ have been performed to estimate the magnitude and the source of the splitting between the symmetric and antisymmetric C=O stretches. It is shown that a large part of the splitting can result from pure electronic coupling mediated via the π -structure of the ligand. Calculations have also been performed on the free ligand malonate⁻ and the neutral malonaldehyde that show decreasing electronic coupling, which is consistent with the decreasing resonance stabilization. A simple effective C=O interaction potential has been produced for $\text{Cl}_2\text{Pt}(\text{malonate})^-$ that is used to estimate the electronic splitting of the 1600 cm^{-1} IR band to 137 cm^{-1} . Anharmonic contributions seem to reduce this value somewhat, but the magnitude and sign of the splitting is similar to the experimental value of 183 cm^{-1} found for the similar $\text{Cl}_2\text{Pt}(\text{acac})^-$ complex.

Introduction

In several infrared studies^{1–3} of transition metal complexes with one or more acetylacetonate ligands (acac^-), it has been observed that the two C=O stretchings in each acac^- ligand seem to be strongly coupled. This coupling is noted as the difference between the symmetric and antisymmetric combinations of the C=O stretch, and it can be seen in most spectra as two peaks around 15 000 cm^{-1} split by 150–300 cm^{-1} .

The assignment and interpretation of the different peaks for acac^- in the C=O stretching region 11 000–17 000 cm^{-1} is complicated by the presence of the C=C stretches, the methyl vibrations, and the C–H bendings. By selectively substituting hydrogen for deuterium at one or more positions in the acac^- ligands, additional information has been obtained; especially, it has been observed that the perturbations of the C=O stretching frequencies are smaller than the C=C ones.

Behnke and Nakamoto^{1,2} studied several square planar Pt(II) complexes with different combinations of Cl and acac^- as ligands. The infrared spectra were recorded, and force field calculations were performed and compared to the spectra. From the study, it was concluded that the splitting of the symmetric and antisymmetric combinations of C=O stretches was not large enough if only independent force constants describing stretch and bending motions were used. Thus, the force field was refined with off-diagonal elements that coupled the two C=O stretches (as well as C=C) so that the symmetric stretch is higher in frequency than the antisymmetric one. The physical reason for this is believed to be the π -conjugation of the electronic structure of acac^- . More recently, the same types of off-diagonal couplings has been successfully employed in other studies, for example by Schönherr et al.³

In this work we will present ab initio calculations of $\text{Cl}_2\text{Pt}(\text{malonate})^-$, which is a complex similar to one studied by Behnke and Nakamoto, $\text{Cl}_2\text{Pt}(\text{acac})^-$. Malonate stands for

the anion of malonaldehyde (dialdehyde form), where one hydrogen has been removed from the central carbon. The full name for the dialdehyde form of malonaldehyde is 1,3-propanedial. The malonate ligand is related to the acetylacetonate by replacement of the two methyl groups with hydrogens.

Both acetylacetone and malonaldehyde exist in two different tautomeric forms (diketo/dialdehyde and enol), depending on the polarity of the solvent. The enol tautomer, where one hydrogen atom from the central carbon is migrated and bonded to the oxygen atoms, is predominant in the gas phase and in non polar solvents, because of the hydrogen-bond stabilization. The enol tautomers of acetylacetone and malonaldehyde are, for this reason, usually written as H(acac) and H(malonate), respectively.

In this work, the C=O stretching motions and possible vibrational coupling mediated by the electronic structure are studied with ab initio methods. For this purpose, calculations of the $\text{Cl}_2\text{Pt}(\text{malonate})^-$ complex, for the bare ligand malonate⁻ ($\text{O}=\text{CH}-\text{CH}-\text{CH}=\text{O}^-$), and the corresponding uncharged malonaldehyde ($\text{O}=\text{CH}-\text{CH}_2-\text{CH}=\text{O}$) have been carried out. These three systems are displayed in Figure 1.

Computational Details

The $\text{Cl}_2\text{Pt}(\text{acac})^-$ complex is a large system, and for this reason, all calculations are done on the smaller $\text{Cl}_2\text{Pt}(\text{malonate})^-$ containing 132 electrons. Reducing the acac^- to malonate⁻ means that a full force field or normal mode calculation is not meaningful since the frequencies will be different. However, the interaction of the C=O stretches should show similar behavior due to the similar electronic structure of acac^- and malonate⁻, having equal number of π -bonds.

As method for calculation, we have chosen the CASSCF procedure⁴, where CASSCF stands for complete active space self-consistent field. To reduce the number of electrons, basis functions on platinum⁵ and

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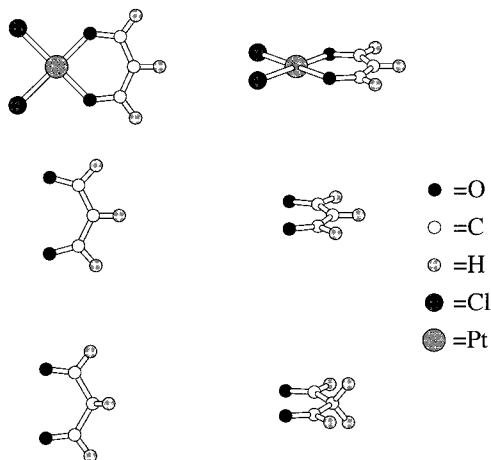


Figure 1. The optimized structures of the three systems treated in this work, from the top $\text{Cl}_2\text{Pt}(\text{malonate})^-$, malonate^- , and malonaldehyde. Each system is displayed from two angles.

chlorine⁶ that include ab initio model potentials (AIMP), together with some relativistic corrections of mass velocity and Darwin type, have been used. In the AIMPs, the core electrons are replaced with nonlocal potentials that include Coulomb and exchange terms as well as relativistic corrections. It should be pointed out that these potentials are determined from all-electron ab initio calculations of the corresponding atom. For the C, O, and H atoms, all electrons basis sets of ANO-S type⁷ were used. The contraction schemes are the following: ANO-S H[7s3p/2s1p], C[10s6p3d/3s2p1d], and O[10s6p3d/3s2p1d]; relativistic AIMP Pt($16e^- = 5p^6 5d^{10}$)[13s10p9d/3s2p2d] and Cl($7e^- = 3s^2 3p^5$)[7s7p1d/2s2p1d]. For the bare ligand malonate^- and the malonaldehyde the same basis sets were used.

In any CASSCF calculations it is necessary to select a number of orbitals and a number of electrons that make up the active space. In this active space, the coefficients of the full CI expansion and the orbitals are optimized iteratively until convergence is achieved. In the malonate^- ligand, the electronic coupling of the vibrational modes should take place mainly through the π -orbitals. In earlier investigations on Rh(II) complexes^{8,9}, it was found that the d-orbitals are rather covalent, and for Pt(II) complexes the same was found.¹⁰ To obtain a good description of the π -orbitals in the acac^- ligand, we wanted to include some of the Pt(II) d orbitals in the active space.

In square planar complexes, the d orbitals are grouped in one pair of degenerate e orbitals and three nondegenerate orbitals. If the ligands are placed along the x- and y-axis, the orbitals that form the e pair are d_{xz} and d_{yz} . The $d_{x^2-y^2}$ orbital, that is directed toward the ligands, has the highest energy and is unoccupied. The d_z^2 and d_{xy} orbitals still remain. In our calculations the complex is close to square planar, but the ligands are placed between the axes in the x,y-plane, see Figure 2. This means that the d_{xy} orbital will be the highest in energy; it is the only of the d orbitals unoccupied (Pt(II)d⁸ low spin). From the remaining doubly occupied orbitals, we expected that the d_{xz} and d_{yz} will interact with the π -system of the malonate^- ligand to form a type of a ring structure; thus these two orbitals were included in the active space. For all calculations, C_s symmetry was used, and then the d_{xz} and d_{yz} orbitals both go into a'' symmetry.

The malonate^- ligand has a π -system that can be defined from the five p_z orbitals centered on the three carbons and the two oxygens. Of these, the three lowest are doubly occupied and the two highest are empty. This set of π -orbitals has an interesting nodal structure^{11,12} that

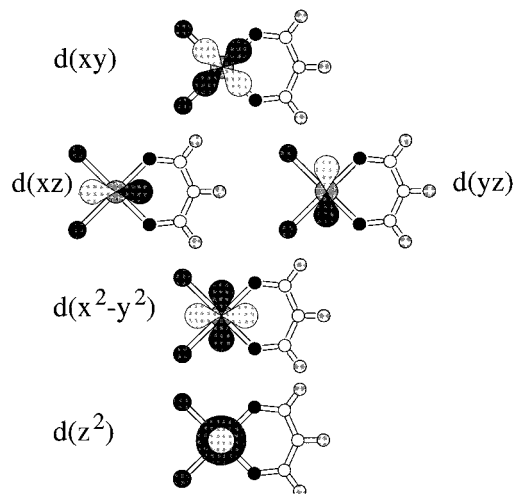


Figure 2. The d orbitals centered on Pt. The four lowest in the figure are doubly occupied, and the highest, $d(xy)$ is unoccupied. Two of the orbitals, $d(xz)$ and $d(yz)$, were included in the CASSCF active space. They are not degenerate for $\text{Cl}_2\text{Pt}(\text{malonate})^-$; however, in true square planar complexes this is the case, and therefore, they are indicated as being similar in energy.

seems to influence different electronic states, as has been shown in another work on $\text{Cr}(\text{malonate})_3$.¹³ The lowest orbital has no nodes (except in the z-plane); the next orbital has one node on the middle carbon, and consequently, the orbital has alternating phase at the two oxygen atoms; then the third orbital, which is the highest occupied, has two nodes and is in-phase on the oxygens. The two unoccupied orbitals have three and four nodes corresponding to out-of-phase and in-phase combinations. All of these five orbitals in a'' symmetry were included in the active space. Plots of the malonate^- orbitals for the transition metal complex $\text{Cr}(\text{malonate})_3$ have been produced elsewhere.¹³

Finally, some test calculations revealed that the lone pair of oxygen plays an important role for the correlation, at least compared to the lower d orbitals d_z^2 and $d_{x^2-y^2}$. Thus, the two occupied and two unoccupied orbitals for the lone pairs of the oxygens were also included in the active space, and all four transform according to a' symmetry.

None of the chlorine orbitals were included in the CASSCF. The chlorine atoms are not directly involved in the high-frequency vibrations due to the large mass, and the calculations revealed a smaller covalency than for the oxygen orbitals.

With these orbitals the active space, $\text{Cl}_2\text{Pt}(\text{malonate})^-$ consists of 14 electrons in 11 orbitals. For the free ligand malonate^- , the active space is the same except for the two metal d orbitals in a'' symmetry, and thus there are 10 electrons in 9 orbitals; for the malonaldehyde the active space is 8 electrons in 8 orbitals, which is a reduction of one orbital and two electrons from the π -system due to the additional hydrogen.

The geometry of the $\text{Cl}_2\text{Pt}(\text{acac})^-$ complex has been obtained by electron diffraction.¹ Since $\text{Cl}_2\text{Pt}(\text{malonate})^-$ is different, we chose to do a full geometry optimization. In addition, vibrational analysis is best performed at the equilibrium geometry produced by the computational procedure. The geometry optimization was performed at the CASSCF level for all three compounds, and the results are displayed in Table 1 and Figure 1.

In empirical force field calculations, the internal coordinates that are used to describe distortions are usually overdetermined. In $\text{Cl}_2\text{Pt}(\text{acac})^-$ with the methyls approximated as one atom, there are 19 in-plane vibrations (11 atoms times two degrees of freedom minus the two translations and one rotation); however, the number of internal coordinates defined as bond lengths and angles are 26. This fact slightly complicates the analysis of the coupling between different distortions.

What we are interested in is to know how strongly the C=O vibrations are coupled. To extract information that is useful in the

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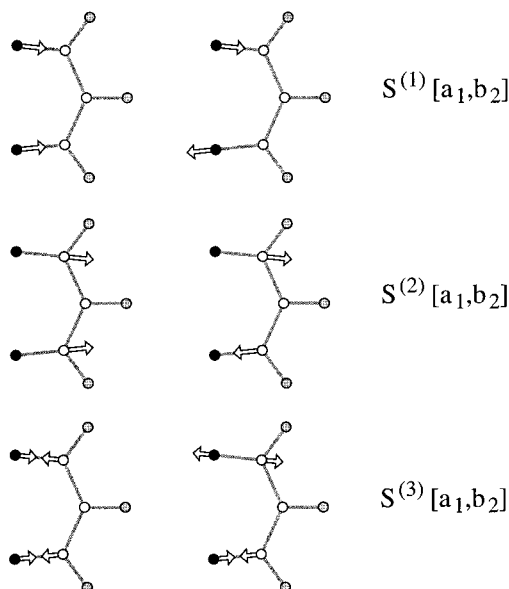


Figure 3. The three types of distortions of the C=O bonds that are used to calculate the force constants in Table 1. The distortions are the same for all three systems, $\text{Cl}_2\text{Pt}(\text{malonate})^-$, malonate^- , and malonaldehyde.

Table 1. The CASSCF Optimized Geometries for the Three Systems

| | $\text{Cl}_2\text{Pt}(\text{malonate})^-$ | malonate^- | malonaldehyde |
|-------------------|---|---------------------|---------------|
| Bond Lengths in Å | | | |
| Pt–Cl | 2.37 | | |
| Pt–O | 2.13 | | |
| O–C | 1.26 | 1.25 | 1.22 |
| C–C | 1.41 | 1.42 | 1.51 |
| C–H(side) | 1.09 | 1.11 | 1.10 |
| C–H(center) | 1.08 | 1.08 | 1.10 |
| Bond Angles | | | |
| Cl–Pt–Cl | 86 | | |
| O–Pt–O | 91 | | |
| O–Pt–Cl | 92 | | |
| C–C–C | 125 | 129 | 120 |
| C–C–O | 129 | 131 | 127 |
| O–C–H(side) | 114 | 116 | 120 |
| C–C–H(center) | 118 | 116 | 105 |

empirical force field calculations, a set of distortions that can be related to the force field constants of the C=O bonds has been performed.

Distortions are defined so that they involve oxygen and carbon (next to oxygen) displacements. The displacements are limited to the direction of the vector connecting carbon and oxygen. With these distortions there are four degrees of freedom. To simplify further, three two-dimensional projections are made from this distortion space. Each of them is defined as being symmetric and antisymmetric with respect to the changes of the two C–O distances. In the first distortion, only the two oxygens are moved along the C–O vector. In the second only the carbons are moved along the C–O direction. In the third, carbon and oxygen are moved simultaneously by the same amount along the C–O axis so as to increase or decrease the C–O distances. With these three symmetric and antisymmetric motions, displayed in Figure 3, there are six potential curves to be calculated for each complex, they are formally described as follows.

If the unit displacement vectors for each of the four atoms are defined as,

$$d_{C_1}, d_{C_2}, d_{O_1}, d_{O_2}$$

and all are directed along the same vector,

$$r_{\text{O}-\text{C}}$$

then the unit vectors of the three two-dimensional projections can be expressed in terms of these displacement vectors. In the first case, the coordinates are

$$s_{a_1}^{(1)} = \frac{1}{\sqrt{2}}(d_{O_1} + d_{O_2}) \quad s_{b_2}^{(1)} = \frac{1}{\sqrt{2}}(d_{O_1} - d_{O_2})$$

In the second case we have,

$$s_{a_1}^{(2)} = \frac{1}{\sqrt{2}}(d_{C_1} + d_{C_2}) \quad s_{b_2}^{(2)} = \frac{1}{\sqrt{2}}(d_{C_1} - d_{C_2})$$

and in the third case,

$$s_{a_1}^{(3)} = \frac{1}{2}(d_{O_1} + d_{O_2} - d_{C_1} - d_{C_2}) \quad s_{b_2}^{(3)} = \frac{1}{2}(d_{O_1} - d_{O_2} - d_{C_1} + d_{C_2})$$

The notation a_1 and b_2 are for C_{2v} symmetry and indicates that the displacements s transform according to the corresponding irreducible representations. As defined above, s is a vector. To expand the potential energy, the total distortion vector, $d(S) = Ss$ is defined, where S is the scalar value of the distortion. The potential energy can then be expanded in a double harmonic expression,

$$V(S_{a_1}, S_{b_2}) = F_{a_1} S_{a_1}^2 + F_{b_2} S_{b_2}^2$$

Clearly, none of the three distortions are normal modes of the complex; however, a calculation of this type makes it possible to directly study differences of symmetric and antisymmetric distortions that involve the C=O bonds without movement of the intermediate carbon atom. The normalization, as defined above, has the effect that if the atoms are uncoupled and moving in independent harmonic potentials of the same strength, the calculated force constant is the same for the mode as for one individual atom.

Results

In Table 2, the calculated CASSCF force constants of the previously defined distortions $s_{a_1}^{(n)}$ and $s_{b_2}^{(n)}$, where $n = 1, 2, 3$, are presented. The unit is $\text{aJ}/\text{Å}^2$, which is related to $\text{cm}^{-1}/\text{Å}^2$ by the relationship $1 \text{ cm}^{-1} = 1.9864 \cdot 10^{-6} \text{ aJ}$.

For the $\text{Cl}_2\text{Pt}(\text{malonate})^-$ complex, it is seen that the highest value of $10.8 \text{ aJ}/\text{Å}^2$ is calculated for the totally symmetrical $s_{a_1}^{(3)}$ distortion involving four atoms. The reason that the value is higher than for the other symmetric modes, $s_{a_1}^{(1,2)}$, is of course because the carbon and oxygen atoms are nearest neighbors and thus couple strongly. The change of the carbon oxygen bond distance is $\sqrt{2}$ times larger than for the other distortions. Comparing the symmetric and antisymmetric distortions (a_1 and b_2 symmetry, respectively) gives about 85% lower values for the antisymmetric distortions. This is a substantial difference considering that the coupling is indirect, either via the Pt atom or via the middle carbon atom. For symmetric types of distortions it seems that the $\text{Cl}_2\text{Pt}(\text{malonate})^-$ complex is more rigid than for antisymmetric distortions.

To study the mechanism operating in the lowering of the antisymmetric modes, we turn to the related free ligand malonate^- and the saturated malonaldehyde. In malonate^- , the C–O bond length decreases from 1.26 to 1.25 Å in $\text{Cl}_2\text{Pt}(\text{malonate})^-$, and the C–C bond length increases from 1.41 to 1.42 Å. These changes indicate that the aromaticity decreases from $\text{Cl}_2\text{Pt}(\text{malonate})^-$ to malonate^- . At the same time, we see that the difference in force constants between symmetric and antisymmetric distortions, 90–94%, is not as large as in $\text{Cl}_2\text{Pt}(\text{malonate})^-$. The reason for the decrease in aromaticity is

Table 2. Calculated CASSCF Force Constants for the Modes s_1 , s_2 , and s_3^a

| Cl ₂ Pt(malonate) ⁻ | | | |
|---|------------|------------|---------|
| | (1) oxygen | (2) carbon | (3) C=O |
| a ₁ | 5.5 | 7.2 | 10.8 |
| b ₂ | 4.9 | 6.0 | 9.1 |
| | 89% | 83% | 84% |
| Malonate ⁻ | | | |
| | (1) oxygen | (2) carbon | (3) C=O |
| a ₁ | 5.4 | 7.0 | 10.8 |
| b ₂ | 5.1 | 6.3 | 9.9 |
| | 94% | 90% | 91% |
| Malonaldehyde | | | |
| | (1) oxygen | (2) carbon | (3) C=O |
| a ₁ | 6.4 | 7.9 | 13.1 |
| b ₂ | 6.4 | 7.9 | 12.7 |
| | 100% | 100% | 97% |

^a From above: the Cl₂Pt(malonate)⁻ complex; the malonate⁻ ligand; and free malonaldehyde. The force constants are given in the unit aJ/Å². The percentage between the symmetric (s_{a_1}) and the antisymmetric (s_{b_2}) force constants is also included.

probably that the π -system including the d orbitals on Pt is closed, while the resonance structures of malonate⁻ are open.

As one proton is attached to the central carbon of malonate⁻ we get the last compound in the study, the dialdehyde form of malonaldehyde. This compound lacks the resonance structures of the previous ones, and indeed, the difference between symmetric and antisymmetric stretches has almost disappeared. The changes in bond lengths follow the trend from Cl₂Pt(malonate)⁻ to malonate⁻, and the C–O distance decreases further, to 1.22 Å, while the C–C is now a single bond 1.51 Å long. In the malonaldehyde, we can compare the distortions of oxygen alone (type $s_{a_1, b_2}^{(1)}$) with currently used values of C–O force constants. The value 6.4 aJ/Å² can be directly related to the empirical ones, since the only bond length affected is C–O. In the book by Hollas,¹⁴ a list of typical values of force constants gives 6.0 aJ/Å² for a C=O double bond (note that values of force constants are defined differently, either with or without a factor of 1/2 in different works). For the malonate⁻ ligand, this value decreases about 20%, to 5.4 aJ/Å² for a_1 or 5.1 aJ/Å² for b_2 .

So far the analysis is within the harmonic approximation. Since it is known that anharmonic effects can be important, we have performed a few vibrational wavefunction calculations using the calculated potentials. In Figure 4, the potentials of the C–O mode (type $s_{a_1, b_2}^{(3)}$) for Cl₂Pt(malonate)⁻ are displayed. One has to remember that these are not proper normal modes of the complex. However, it is generally believed that the C–O vibrations are local and, therefore, are not strongly coupled to the movement of the other atoms in the complex. Our simplified analysis of the anharmonicity proceeds as follows. First, we create an effective C–O interaction; the curves in Figure 4 are used for this. For each unit of increment of the two modes, the real C–O distance changes with the same amount in Å. Thus, dividing the energy by two gives an effective potential for a system consisting of two atoms, C and O, with an effective bonding interaction. The reduced mass for this system is (12)(16)/(12 + 16) = 6.86 au.

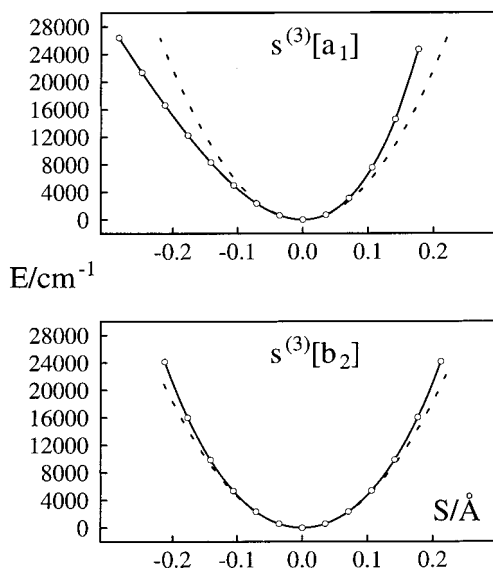


Figure 4. The potential energy of the symmetric $s_{a_1}^{(3)}$ and antisymmetric $s_{b_2}^{(3)}$ distortions for Cl₂Pt(malonate)⁻. The circles are the ab initio points and the solid curves are cubic splines of the points. The dashed curves are the second-order harmonic potential with the following force constants, 10.8 aJ/Å² for $s_{a_1}^{(3)}$ and 9.1 aJ/Å² for $s_{b_2}^{(3)}$.

Table 3. The Vibrational Wavefunction Calculations for the Effective C=O System Described in the Text

| n | Cl ₂ Pt(malonate) ^{- a} | |
|-------------------|---|-----------------|
| | $(E_{n+1} - E_n) / \text{cm}^{-1}$ | |
| | $s_{a_1}^{(1)}$ | $s_{b_2}^{(1)}$ |
| E_{harm} | 1629 | 1495 |
| $2E_{\text{zp}}$ | 1622 | 1507 |
| 1 | 1610 | 1521 |
| 2 | 1595 | 1547 |
| 3 | 1580 | 1571 |
| 4 | 1551 | 1594 |

^a The values are the energy spacings between the different levels in cm^{-1} . The energy E_{harm} is calculated from the harmonic force constant, the energy $2E_{\text{zp}}$ is the calculated vibrational zero point energy multiplied with two, the others $n = 1, 2, 3, 4$ give energy differences between vibrational wavefunctions.

With the effective potential and the reduced mass, it is possible to calculate a vibrational wavefunction and energies with a discrete variable Hamiltonian⁹, which is explained in the appendix. In Table 3 and Figure 5, the result of this vibrational calculation is shown. With the harmonic approximation, the energies are 1629 (symmetric) and 1495 cm^{-1} (antisymmetric), and the splitting is 134 cm^{-1} . With the nuclear wavefunction, thus including anharmonicity, the splitting decreases. The symmetric distortion has decreasing spacings with increasing quantum number, while the antisymmetric increases the spacings. The zero point energy multiplied by two is calculated to 1622 (a_1) and 1507 (b_2) cm^{-1} , giving a splitting of 115 cm^{-1} , and the first energy differences, 1610 (a_1) and 1522 (b_2), give a splitting of 88 cm^{-1} (1 on the x-axis in Figure 5).

In the work of Behnke and Nakamoto on the Cl₂Pt(acac)⁻ complex, the C=O stretching frequencies are assigned in the spectrum to peaks at 1563 (a_1) and 1380 (b_2) cm^{-1} , giving a splitting of 183 cm^{-1} . This value agrees reasonably with the calculated splitting of the harmonic part of the potential, 134 cm^{-1} , but not with the one including the full anharmonic potentials, 88 cm^{-1} . Since the molecules are different and we are not calculating normal modes, this is not surprising, probably

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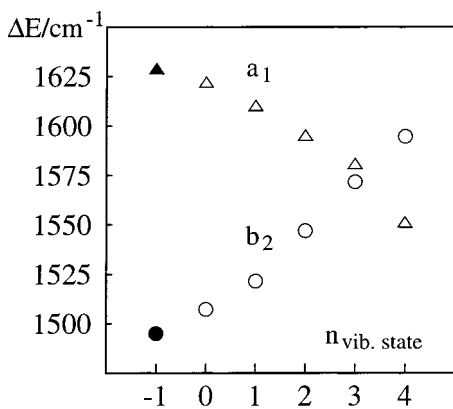


Figure 5. The energy spacings of the nuclear wavefunction on the effective C=O potentials for the symmetric and antisymmetric distortions (Figure 3). The filled dots and triangle are the energy spacings calculated from the harmonic force constants 10.8 (a_1) and 9.1 (b_2) $\text{aJ}/\text{\AA}^2$, symmetric and antisymmetric distortions, symbolically placed at $n = -1$. The open dots and triangles correspond to the energy spacing of the nuclear wavefunctions. The numbering on the x -axis defines: $n = 0$, the zeropoint energy multiplied with two $2E_0$; $n = 1$, the energy difference between the lowest state and second state $E_1 - E_0$, 2,3... the following energy differences.

the anharmonicity is overestimated. It seems however, that we can conclude that there is a large electronic coupling between symmetric and antisymmetric distortions for this type of systems, and that the coupling results from the resonance structures of the π -system. This confirms the early conclusions of Behnke and Nakamoto, that one has to include next nearest neighbor couplings via the middle carbon in any realistic force field calculation of the $\text{Cl}_2\text{Pt}(\text{malonate})^-$ complex. It is also in accordance with the infrared measurements of Schönherr, Rosellen, and Schmidtke³ on $\text{Sn}(\text{acac})\text{Cl}_4^-$ and $\text{Sb}(\text{acac})\text{Cl}_4^-$, where splittings of the same order of magnitude were found for both complexes with different combinations of deuteration.

Summary and Conclusions

In this work we have presented an analysis of the dynamics of the two C–O bonds in $\text{Cl}_2\text{Pt}(\text{malonate})^-$, the free ligand malonate⁻ $\text{O}=\text{CH}-\text{CH}-\text{CH}=\text{O}^-$, and the dialdehyde form of malonaldehyde $\text{O}=\text{CH}-\text{CH}_2-\text{CH}=\text{O}$. In particular, the electronic coupling via the π -conjugated system has been shown to influence the strength of the C–O force constant in such a way that the antisymmetric type of distortion, where one C–O bond distance increases and the other decreases, is lower in energy than the symmetric one. The difference in force constant is estimated to be around 15% for $\text{Cl}_2\text{Pt}(\text{malonate})^-$, 10% for malonate⁻, and 2% for the malonaldehyde. The electronic resonance structures are probably responsible for the coupling as indicated by the trend.

Furthermore, we have analyzed the anharmonic contributions to the symmetric and antisymmetric vibrations of the C–O bonds. Compared to the harmonic approximation, the effect on the symmetric distortion is a decrease of the energy spacing, and the effect on the antisymmetric is an increase of the energy spacing. The anharmonicity is working in the opposite direction of the electronic coupling; it slightly decreases the splitting of the symmetric and antisymmetric modes.

The calculations we have performed should be seen as a complement to straightforward normal-mode analysis, and they confirm the early conclusions of Behnke and Nakamoto,^{1,2} that there must be a strong electronic effect operating in the $\text{Cl}_2\text{Pt}(\text{acac})^-$ system caused by the conjugated π -bonds.

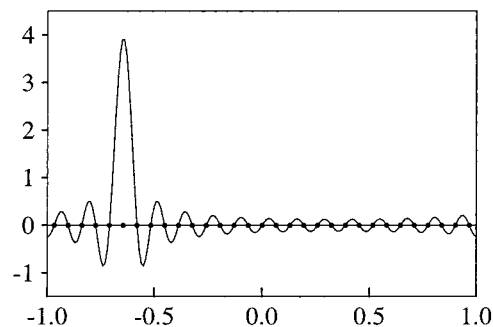


Figure 6. One of the maximally localized functions, $|x_j\rangle$.

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Appendix: Calculation of the Vibrational Wavefunction

To numerically solve the vibrational wavefunction on a one-dimensional potential, the following procedure was used. The $N = 2n + 1$ basis functions are the trigonometric functions expressed as exponentials, and the interval where the wavefunction is defined is $x = \{-a/2, a/2\}$ a box of length a . Note that $i = \sqrt{-1}$.

$$f_k(x) = \frac{1}{\sqrt{a}} e^{i2\pi kx/a}, \quad k = -n, \dots, n$$

$$\langle f_k | f_l \rangle = \frac{1}{a} \int_{-a/2}^{a/2} e^{-i2\pi kx/a} e^{i2\pi lx/a} dx = \delta_{k,l}$$

To calculate the potential energy integrals, we transform the above functions to a maximally localized and completely real form, centered on $x_j = aj/N$, $j = -n, \dots, n$ (in Figure 6, this function is shown for; $a = 2.0$, $n = 15$ and centered on $j = -10$),

$$|x_j\rangle = \frac{1}{\sqrt{N}} \sum_{k=-n}^n f_k \left(x - \frac{ja}{N} \right) = \frac{1}{\sqrt{N}} \sum_{k=-n}^n |f_k\rangle e^{-i2\pi kj/N}$$

The functions are also called Dirichlet kernel functions and can be written in closed form $|x_j\rangle = 1/\sqrt{N} \sin(Nt)/\sin(t)$, $t = \pi/a(x - ja/N)$. They are orthogonal as can be checked,

$$\langle x_l | x_j \rangle = \frac{1}{N} \sum_{k=-n}^n \sum_{k'=-n}^n \langle f_k | f_{k'} \rangle e^{i2\pi k(l-j)/N} = \frac{1}{N} \sum_{k=-n}^n e^{i2\pi k(l-j)/N} = \delta_{l,j}$$

where the last sum is the discrete Fourier transform of an exponential so that the delta function results. The sum can be evaluated by noting the similarity to the expression, $(b - 1) \sum_{k=-n}^n b^k = b^{n+1} - b^{-n} = b^{-n}(b^{2n+1} - 1)$, where $b^k = (e^{i2\pi(l-j)/N})^k$. The sum $\sum_{k=-n}^n b^k$ must be zero for $|l - j| = 1, 2, 3, \dots, 2n$ since then $b^{2n+1} - 1 = 0$ and $b - 1 \neq 0$; otherwise for $|l - j| = 0$, $2n + 1$ the sum equals N .

With the localized functions, $|x_j\rangle$, the potential operator can be set as diagonal for sufficiently large n ,

$$\langle x_l | V(x) | x_j \rangle = \delta_{l,j} V(x_j), \quad x_j = \frac{ja}{N}$$

where $V(x_j)$ is the potential at the point x_j . The second derivative operator is calculated as follows,

$$\begin{aligned} \left\langle x_l \left| \frac{\partial^2}{\partial x^2} \right| x_j \right\rangle &= \frac{1}{N} \int_{-a/2}^{a/2} \sum_{k=-n}^n \sum_{k'=-n}^n - \\ &\quad \left(\frac{2\pi k}{a} \right)^2 f_k^* f_{k'} e^{i2\pi(k'l - kj)/N} dx = \\ &= -\frac{1}{N} \left(\frac{2\pi}{a} \right)^2 \sum_{k=-n}^n k^2 e^{i2\pi k(l-j)/N} = \\ &\quad -\frac{1}{N} \left(\frac{2\pi}{a} \right)^2 2 \sum_{k=1}^n k^2 \cos[2\pi k(l-j)/N] \end{aligned}$$

It is possible to write the kinetic energy operator K as follows,

$$K(|l-j\rangle) = \left\langle x_l \left| -\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} \right| x_j \right\rangle$$

and K only depends on the absolute value of $|l-j|$ and the number of spacings between basis function $|x_l\rangle$ and $|x_j\rangle$ so that it can be represented as a vector (including the reduced mass in atomic units, where the electron has mass 1 au and the proton 1836.15 au),

$$K(j) = \frac{1}{N\mu} \left(\frac{2\pi}{a} \right)^2 \sum_{k=1}^n k^2 \cos[2\pi kj/N] \quad j = 0, \dots, 2n$$

In this way the one-dimensional Schrödinger equation (atomic units of length is $1 \text{ \AA} = 0.52917 \text{ au}$),

$$-\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} \Psi(x) + V(x)\Psi(x) = E\Psi(x)$$

is numerically solved for the energies E by diagonalizing the Hamiltonian matrix,

$$H_{lj} = V(x_j)\delta_{lj} + K(|l-j|)$$

In the calculations for the C=O stretching, n was chosen to 75. The total number of basis functions were $N = 2n + 1 = 151$, labeled with $j = -75, \dots, 0, \dots, 75$.

It was necessary to include the potential curve up to about $24\,000 \text{ cm}^{-1}$ in order to converge the calculations for the lowest states, even though their energies were below $10\,000 \text{ cm}^{-1}$. This is due to the "tunneling" of the vibrational wavefunction and is an effect of the small mass and strong spring constant. This effect is less pronounced for heavier atoms or smaller force constants.

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