Lattice dynamics of $\alpha$-CO from an ab initio potential

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Harmonic lattice dynamics calculations have been performed for the antiferroelectric $P2_{1}3$ ordered phase of $\alpha$-carbon monoxide and for two related structures with a different head–tail ordering of the CO molecules. The potential used is an ab initio CO–CO potential with its anisotropy expanded in spherical harmonics, as well as a site–site model fitted to this ab initio potential. Good agreement with experiment is obtained for the structure, the cohesion energy, and the phonon frequencies without any adjustment of the potential. Head–tail reordering of the molecules is energetically almost neutral if it is accompanied by a translational displacement along the bond axes, which is symmetric with respect to the inversion centers of the average $Pa3$ structure. This displacement is induced in particular by the strong head–tail anisotropy in the short-range repulsion. Translation–rotation coupling is found to be important; it affects especially the frequency of the lowest optical mode.

I. INTRODUCTION

Solid CO is a simple molecular crystal, but it still raises essential questions. Under its own equilibrium pressure, it exists in two stable phases. The high temperature $\beta$ phase ($61.5 < T < 68.1$ K) has a hexagonal lattice in which the molecules are orientationally disordered, just as in $\beta$ nitrogen. It is typical, however, that the order–disorder transition temperature in CO is much closer to the melting temperature than it is in $N_2$. At temperatures below 61.5 K, carbon monoxide crystallizes in the orientationally ordered $\alpha$ phase. This phase has a cubic crystal structure with four molecules in the unit cell, just like $\alpha$ nitrogen (space group $Pa3$). Calorimetric measurements show, however, that there is a residual entropy that is even of random head–tail disorder of the CO molecules in this phase. From mean-field calculations that use only the small dipole moments of the CO molecules, it is estimated that the head–tail ordering temperature is as low as 5 K. Dielectric, nuclear quadrupole resonance (NQR), and nuclear magnetic resonance (NMR) measurements have revealed two reordering processes—relatively fast head–tail flips and slow translational–rotational jumps in which the molecule goes into a neighboring site, but well above the ordering temperature, both reordering processes become extremely slow, so that the head–tail disorder persists even at very low temperatures. The fully ordered ground state, which is probably antiferroelectric with space group $P2_{1}3$ ($T^4$), can therefore not be observed. There is a short-range antiferroelectric order, however.

The main questions are the following: what is the head–tail asymmetry in the long- and the short-range parts of the intermolecular potential of CO and how does this asymmetry affect the head–tail (dis)order and the properties of the $\alpha$ phase? In the earlier lattice dynamics calculations on $\alpha$-CO, the head–tail asymmetry was completely neglected. The empirical model potentials used were the same as in solid nitrogen, with only the values of the parameters slightly readjusted. In the calculations of Okray-Hall and James, the model potential was still symmetric with respect to the midpoint of the CO bond axis, but the mass asymmetry was already included. Fracassi et al. obtained an asymmetric pair potential partly from quantum chemical calculations, which was modeled and then fitted to the lattice energy and the phonon frequencies of $\alpha$-CO. Recently, in our group, an ab initio CO pair potential has been obtained. The anisotropy of this potential was represented directly by an expansion in spherical harmonics. In the present harmonic lattice dynamics study of $\alpha$-CO, we use this potential without any readjustment. We also fit a site–site model to the $ab$ initio potential and we investigate the influence of the approximations inherent in this model. As was pointed out already by Fracassi et al., one may expect important effects of translation–rotation coupling in solid CO. We evaluate these effects explicitly.

In all previous lattice dynamics calculations on $\alpha$-CO and also in ours, the fully ordered $P2_{1}3$ structure has been considered (see Fig. 1). If the centers of the molecules are on the lattice positions of the face-centered-cubic (fcc) lattice and if one averages over the two possible head–tail orientations, the lattice positions become inversion centers and the average structure has the $Pa3$ symmetry. We find that the molecules are actually shifted, however, and that the situation is somewhat more complex. We have not only performed calculations on the fully ordered $P2_{1}3$ structure, but also on two closely related structures. In one structure, the molecules in one of the four sublattices are inverted with respect to the $P2_{1}3$ structure, and in the other structure, the molecules of two sublattices are inverted. All possible combinations of inverted molecules in the unit cell are equivalent to one of these three structures. By comparing the results for the three structures, we obtain more information on the influence of the head–tail order of the CO molecules on the lattice dynamics.

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II. THE AB INITIO POTENTIAL

A. Spherical expansion

The \textit{ab initio} potential used in the calculations is an anisotropic CO pair potential.\textsuperscript{14} Its anisotropy is represented explicitly by means of the expansion

\[ V(R, \hat{r}_A, \hat{r}_B) = \left( 4\pi \right)^{3/2} \sum_{L_A, L_B, l} V_{L_A, L_B, l}(R) A_{L_A, L_B, l}(\hat{r}_A, \hat{r}_B), \]

where \( A_{L_A, L_B, l} \) forms a complete orthonormal set of angular functions

\[ A_{L_A, L_B, l}(\hat{r}_A, \hat{r}_B) = \sum_{M_A, M_B, M} \left( \begin{array}{ccc} L_A & L_B & L \\ M_A & M_B & M \end{array} \right) \times Y_{L_A, M_A}(\hat{r}_A) Y_{L_B, M_B}(\hat{r}_B) Y_{LM}(\hat{R}). \]

The vector \( R = (R, \hat{R}) \), points from the center of mass of molecule \( A \) to that of molecule \( B \), the unit vectors \( \hat{r}_A = (\theta_A, \phi_A) \) and \( \hat{r}_B = (\theta_B, \phi_B) \) describe the orientations of the respective molecular axes. The functions \( Y_{lm}(\hat{r}) \) are spherical harmonics and the symbol in large brackets is a 3-j coefficient. All orientations are given with respect to an arbitrary frame, which may be fixed to the lattice in this case. The expansion coefficients are the sum of an electrostatic, an exchange, and a dispersion contribution

\[ V_{L_A, L_B, l}(R) = V_{L_A, L_B, l}^{\text{elec}}(R) + V_{L_A, L_B, l}^{\text{exch}}(R) + V_{L_A, L_B, l}^{\text{disp}}(R). \]

The very small induction effects are neglected. The expansion has anisotropic terms up to \( L_A + L_B = 5 \) with \( L_A + L_B \leq 9 \).

The electrostatic contribution to the expansion coefficients is directly given by the well-known multipole expansion

\[ V_{L_A, L_B, l}^{\text{elec}}(R) = \left( -1 \right)^{L_B} S_{L_A + L_B, l} \left[ \frac{(2L_A + 2L_B)!}{(2L_A + 1)!(2L_B + 1)!} \right]^{1/2} \times Q_{L_A} Q_{L_B} R^{-L_B - 1}, \]

where \( Q_{L_a} \) and \( Q_{L_b} \) are the multipole moments of molecules \( A \) and \( B \). The multipole moments used in this potential are given in Table I. They were calculated by the self-consistent field (SCF) method, except for the dipole moment where the experimental value was used.\textsuperscript{14}

The exchange contribution to the intermolecular potential has been calculated using the Heitler–London formula for 180 orientations of the molecules at three intermolecular distances \( R = 5.5, 6.5, \) and \( 7.5 \) bohr. The expansion coefficients for the exchange interaction at these distances were obtained directly from these calculations, by the procedure described in Ref. 14. Their distance dependence is given by an exponential function

\[ V_{L_A, L_B, l}^{\text{exch}}(R) = \frac{V_{L_A, L_B, l}^{\text{exch}}(R_0)}{\exp \left[ -\alpha_{L_A, L_B} (R - R_0) \right]}, \]

with \( R_0 = 6.5 \) bohr. In order to obtain the coefficients \( a_{L_A, L_B} \) needed for the damping functions of the dispersion interactions (see below), a second fit of the distance dependence was made

\[ V_{L_A, L_B, l}^{\text{exch}}(R) \approx \frac{V_{L_A, L_B, l}^{\text{exch}}(R_0)}{\exp \left[ -\alpha_{L_A, L_B} (R - R_0) \right]}. \]

The dispersion contribution to the expansion coefficients has been written as

\[ V_{L_A, L_B, l}^{\text{disp}}(R) = -\sum_{n=0}^{\infty} f_n^{L_A, L_B, l}(R) C_n^{L_A, L_B, l} R^{-n}, \]

where \( C_n^{L_A, L_B, l} \) are anisotropic long-range dispersion coefficients that have been taken from accurate \textit{ab initio} calculations by Rijks and Wormer.\textsuperscript{15} The functions \( f_n^{L_A, L_B, l}(R) \) are damping functions similar to the form by Tang and Toennies\textsuperscript{16}

\[ f_n^{L_A, L_B, l}(R) = 1 - \left[ \sum_{k=0}^{n} \left( \frac{a_{L_A, L_B} R}{k!} \right)^k \right] \exp \left[ -a_{L_A, L_B} R \right], \]

where the coefficients \( a_{L_A, L_B} \) are obtained from the first-order exchange repulsion [see Eq. (6)].

All the parameters that characterize this potential are tabulated in Ref. 14. The head–tail asymmetry is reflected by the terms in the spherical expansion with odd \( L_A \) and/or \( L_B \). It is illustrated in Ref. 14 that there is an important asymmetry in the exchange repulsion—the C atom is considerably

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Multipole} & \textbf{Value} \\
\hline
Dipole & \( 1 \) \\
Quadrupole & \( 2 \) \\
Octupole & \( 3 \) \\
Hexadecapole & \( 4 \) \\
32-pole & \( 5 \) \\
\hline
\end{tabular}
\caption{Multipole moments of the CO molecule in \( e\alpha_0^2 \).}
\end{table}
“larger” than the O atom. This effect is reinforced by the fact that the C atom is further away from the CO center of mass than the O atom. For instance, the repulsion for linear OC–CO is about ten times larger than for linear CO–OC at equal center-of-mass distance $R$. It is worthwhile to mention also that this potential yields a second virial coefficient for CO that is within the experimental error bars over a wide temperature range. The anisotropic contribution to this virial coefficient is certainly not negligible (see Ref. 14).

**B. Site–site potential**

In previous lattice dynamics calculations, the interaction potential between the CO molecules has been approximated by an atom–atom or site–site model. The intermolecular pair potential is then written as the sum of (isotropic) interactions between the carbon and the oxygen atoms or between (additional) sites on the CO bond axes

$$V_{AA} = \sum_{i} \sum_{j} c_{ij}^{AA} \exp(-B_{ij} R_{ij}), \quad (9)$$

where $c_{ij}^{AA}$ is the interaction between site $i$ on molecule $A$ and site $j$ on molecule $B$. Here, we assume that the site–site potential consists of an electrostatic, an exchange, and a dispersion contribution, and we fit these contributions to the corresponding terms in the spherical expansion of the $ab$ initio potential.

For the exchange interactions, we have chosen two sites on the molecular axis and the interaction between these sites is expressed as

$$v_{ij}^{\text{exch}}(R_{ij}) = A_{ij} \exp(-B_{ij} R_{ij}), \quad (10)$$

where $R_{ij}$ is the distance between the interaction sites. The positions of the sites on the molecular axis $(r_{i}$ and $r_{j})$ and the exchange parameters $(A_{ij}$ and $B_{ij})$ are found by fitting the site–site exchange interaction to the exchange contribution in the spherical expansion. In this fit procedure, we have used the same grid of 540 dimer geometries that was used for the calculation of the exchange in the spherical expansion. The results of this fit are presented in Table II. The root-mean-square deviation from the spherical expansion is 5.0%.

The dispersion contribution to the site–site potential is expressed as

$$v_{ij}^{\text{disp}}(R_{ij}) = -f_{ij}^{\text{disp}}(R_{ij}) \exp(-B_{ij} R_{ij}), \quad (11)$$

In order to fit this interaction to the dispersion contribution in the spherical expansion, we have again used two interaction sites with optimized positions on the molecular axis. The damping function $f_{ij}^{\text{disp}}(R_{ij})$ is given by

$$f_{ij}^{\text{disp}}(R_{ij}) = 1 - \left[ \sum_{k=0}^{n} \frac{(B_{ij} R_{ij})^k}{k!} \right] \exp(-B_{ij} R_{ij}), \quad (12)$$

where $B_{ij}$ are the parameters obtained from the exchange fit [see Eq. (10)]. We have used the same set of orientations as in the fit of the exchange part, but the intermolecular distances were somewhat larger: $R = 6.5$, 7.5, and 8.5 bohr. The parameters obtained from this fit are also given in Table II. The root-mean-square deviation in the fit of the dispersion energy was 6.5%.

The electrostatic contribution to the site–site potential is represented by three point charges on the CO bond axis— one on the oxygen atom, one on the carbon atom, and one in the center of mass. These point charges were chosen such that the dipole and quadrupole moments of the CO molecule are reproduced. They are given in Table II. Additional freedom in the positions of the point charges in order to reproduce also the octupole and hexadecapole moments exactly did not significantly improve the fit of the total electrostatic interactions.

**III. LATTICE DYNAMICS CALCULATIONS AND RESULTS**

The lattice dynamics calculations are made in the standard harmonic approximation. The formulas required to use a potential in the spherical expansion have been derived in Ref. 17. We assume five degrees of freedom per CO molecule, three translational and two rotational ones. The internal stretch vibration of the molecule is frozen. This assumption is justified because of the large difference in energy. The stretching frequency in the free CO molecule is 2143 cm$^{-1}$, while the phonon frequencies are all below 100 cm$^{-1}$. The intermolecular interaction is calculated for distances up to 12.0 Å which corresponds with lattice sums over 176 molecules. The exchange interaction in the spherically expanded potential could already be truncated at $R = 8.1$ Å.

In the calculations with the site–site potential, the electrostatic interactions are summed by the Ewald method. The difference between the results of the Ewald summation and the results obtained from direct summation of the electrostatic terms is minute. The splittings between the longitudinal and transversal components of the optical modes in the cubic phase (LO–TO splittings) which are obtained by the Ewald method are all smaller than 0.15 cm$^{-1}$. Also the difference in the static lattice energy is negligible. This good convergence of the direct summation of the electrostatic interactions is due to the small dipole moment of the CO molecules. In the calculations with the spherical expansion of the potential, we use only the direct summation.

**A. The $P2_{1}3$ structure**

Given the symmetry of this structure, we can optimize the cubic lattice constant and the positions of the molecules on the body diagonals. The lattice constant obtained by
minimization of the static lattice energy is 5.658 Å for the spherically expanded potential and 5.628 Å for the site–site potential. For both potentials, the CO molecules are shifted along the body diagonals in the direction of the oxygen atoms. For the spherically expanded potential, the shift of the center of mass from the centrosymmetric lattice sites is 0.31 Å and for the site–site potential, it is 0.13 Å. The static lattice energies, split into different contributions, are given for both potentials in Table III. The deviations between the spherical expansion and the site–site model fit to this expansion are small. The difference in the total lattice energy is 7%, the differences in the individual contributions are less than 4%.

In order to investigate the effect of translation–rotation coupling on the lattice modes, we have calculated the lattice frequencies with the spherically expanded potential for the pure translational degrees of freedom, for the pure rotational degrees of freedom, and for both together. The lattice frequencies from these three calculations are compared in Table IV. We find strong mixing of the translations and librations and substantial shifts of the phonon frequencies. Especially the lowest librational (E) mode drops considerably in frequency (from 54.0 to 35.8 cm$^{-1}$) by the admixture of translational character. The explanation of this effect is discussed below. In Table V, we compare the lattice frequencies with the measured Raman and infrared frequencies with the spherically expanded potential. The phonon dispersion curves for the P2$_3$ structure calculated with both potentials are given in Figs. 2 and 3.

B. Other structures

We have investigated the effect of head–tail flips of the CO molecules by making lattice dynamics calculations on a structure in which all the molecules in one of the four sublattices are inverted. The space group of this structure is P3. We have optimized this structure with respect to the static lattice energy and found that the unit cell remains cubic. The orientations of the molecules in the three symmetry-related sublattices are not exactly along the body diagonals; they are rotated by about five degrees. The static lattice energy is — 2.297 kcal/mol at a lattice constant of 5.645 Å (with the spherically expanded potential). If we compare this with the static lattice energy for the P2$_3$ structure, we observe that the P3 structure is slightly lower in energy. All the energy components contribute to this difference, in about the same ratio in which they contribute to the total lattice energy (see Table III). It is questionable whether this small difference (only 1.4% of the lattice energy) is significant, but the fact that it is so small is interesting since this indicates that the head–tail flips of the CO molecules, although they are hindered by a high activation barrier, are energetically almost neutral. In all sublattices, the molecules are again shifted (by 0.28 and 0.35 Å) along the body diagonals in the direction of the oxygen atoms. Table V compares the lattice frequencies calculated at the T point with those calculated for the P2$_3$ structure. The differences are small. The triply degenerate T modes are split into a doubly degenerate E mode and an A mode.

In the third structure that we have investigated, the molecules of two sublattices are inverted. Minimization of the static lattice energy yields an orthorhombic lattice with $a = 5.961$ Å, $b = 5.395$ Å, and $c = 5.492$ Å. The molecules lie on the centers of the faces of the unit cell; their orientations are parallel to the ac plane. The angles of the molecular axes with the c axis are 41° for the molecules of sublattices 1 and 2, and 139° for the molecules of sublattices 3 and 4. The shifts along the molecular axes are 0.32 Å in the direction of the oxygen atoms for all the molecules. The static lattice energy is $-2.33$ kcal/mol. This value is even lower than the lattice energies of the P2$_3$ and P3 structures, but we have also estimated the zero-point vibrational energies for the different structures and found that the lower static energy is compensated by a higher zero-point energy. All the lattice modes in this structure are nondegenerate with frequencies between 20 and 140 cm$^{-1}$. This third structure turns out to be so different from the observed (average) P43 structure, however, that it is only of theoretical interest.

IV. DISCUSSION AND CONCLUSIONS

If we compare the optimized P2$_3$ structure that we have obtained using the $ab initio$ potential with the experimental structure, we observe that the agreement is very good. The measured lattice constant is 5.646 Å at 8 K, while we have calculated 5.658 Å for the spherically expanded potential and 5.628 Å for the site–site potential. Also the cohesion energy (see Table III) agrees well with the experimental value. The shift of the CO molecules along the body diagonals was estimated by Vegard and by Krupskii et al. by fitting calculated x-ray intensities to the experimental data. Vegard calculated the shift to be 0.20 Å and Krupskii et al.

### Table III. Static lattice energy (in kcal/mol).

<table>
<thead>
<tr>
<th>Spherical expansion</th>
<th>Site–site potential</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant $a$ (Å)</td>
<td>5.658</td>
<td>5.628</td>
</tr>
<tr>
<td>Exchange</td>
<td>1.945</td>
<td>1.933</td>
</tr>
<tr>
<td>Dispersion</td>
<td>3.673</td>
<td>3.804</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>0.536</td>
<td>0.557</td>
</tr>
<tr>
<td>Total</td>
<td>2.265</td>
<td>2.428</td>
</tr>
</tbody>
</table>

$^*$At 8 K (Ref. 4).

$^*$Cohesion energy $= 1.987$ kcal/mol (Ref. 21), corrected with the zero-point lattice vibration energy 0.493 kcal/mol (Ref. 13).

### Table IV. Lattice frequencies (in cm$^{-1}$) in the P2$_3$ structure, calculated with the spherically expanded $ab initio$ potential.

<table>
<thead>
<tr>
<th>Character</th>
<th>Coupled</th>
<th>Translations only</th>
<th>Liberations only</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.0 (E)</td>
<td>35.8 (E)</td>
<td>5.646</td>
<td>62% $L$–38% $T$</td>
</tr>
<tr>
<td>57.6 (T)</td>
<td>45.7 (T)</td>
<td>5.646</td>
<td>62% $L$–38% $T$</td>
</tr>
<tr>
<td>56.4 (A)</td>
<td>56.4 (A)</td>
<td>5.628</td>
<td>100% $T$</td>
</tr>
<tr>
<td>57.9 (T)</td>
<td>62.0 (T)</td>
<td>5.628</td>
<td>23% $L$–77% $T$</td>
</tr>
<tr>
<td>62.5 (E)</td>
<td>74.4 (E)</td>
<td>5.628</td>
<td>38% $L$–62% $T$</td>
</tr>
<tr>
<td>83.9 (T)</td>
<td>87.2 (T)</td>
<td>5.628</td>
<td>23% $L$–77% $T$</td>
</tr>
<tr>
<td>97.3 (T)</td>
<td>98.3 (T)</td>
<td>5.628</td>
<td>92% $L$–8% $T$</td>
</tr>
</tbody>
</table>
TABLE V. Lattice frequencies (in cm\(^{-1}\)) at \(q = 0\), calculated for different structures (P\(2_{\overline{3}}\,3\) and P\(3\)) and different potentials (SE = \textit{ab initio} potential in the spherical expansion, SS = site-site model fitted to the \textit{ab initio} potential).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>P(2_{\overline{3}}) (SE)</th>
<th>P(3) (SE)</th>
<th>P(2_{\overline{3}},3) (SS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman(^{a})</td>
<td>38</td>
<td>34.3 ((E))</td>
<td>33.0 ((E))</td>
</tr>
<tr>
<td>Raman(^{a}) (strong)</td>
<td>44</td>
<td>42.5 ((A))</td>
<td>44.3 ((T_{\text{trans}}))</td>
</tr>
<tr>
<td>Raman(^{a})</td>
<td>58</td>
<td>56.9 ((A))</td>
<td>62.1 ((A))</td>
</tr>
<tr>
<td>Infrared, Raman(^{a})</td>
<td>49, 50.5, 52</td>
<td>58.2 ((E))</td>
<td>57.0 ((T_{\text{trans}}))</td>
</tr>
<tr>
<td>Raman(^{a})</td>
<td>64.5</td>
<td>70.8 ((E))</td>
<td>76.6 ((E))</td>
</tr>
<tr>
<td>Infrared(^{a})</td>
<td>85, 86</td>
<td>86.5 ((E))</td>
<td>90.6 ((T_{\text{trans}}))</td>
</tr>
<tr>
<td>Raman(^{a}) (strong)</td>
<td>90.5</td>
<td>97.2 ((A))</td>
<td>119.1 ((T_{\text{long}}))</td>
</tr>
</tbody>
</table>

\(^{a}\)From Ref. 18.
\(^{b}\)From Refs. 19 and 20.

al. found the best agreement between measured and calculated intensities with a shift of 0.08 Å. The latter value is just the distance between the midpoint of the CO bond axis and the CO center of mass. Both experimentalists found that the shifts are in the direction of the oxygen atoms. The shifts that we have calculated for both potentials, in the P\(2_{\overline{3}}\,3\) structure as well as in the other two structures, are also in the direction of the oxygen atoms and they are of the same order of magnitude as measured. We have found that the size of this shift is very sensitive to the potential.

Previous lattice dynamics calculations by Okray-Hall and James\(^1\) used an effective homonuclear potential. The shifts which they obtained from the mass asymmetry of the CO molecules are mostly in the wrong direction.\(^1\) So it is essential that the intermolecular potential is intrinsically asymmetric with respect to the head–tail flips of the CO molecules. The shift calculated by Fracassi \textit{et al.}\(^12,13\) is 0.14 Å. The shift of the CO molecules in the direction of the oxygen atoms is caused in particular by the strong asymmetry in the exchange repulsion. As discussed in Sec. II A, it follows from the \textit{ab initio} potential that the C atoms are substantially “larger” than the O atoms.

The observations may possibly be clarified by introducing a molecular “center of interaction,” which more or less coincides with the “center of electronic charge distribution.” The position of such a center on the CO bond axis can be defined (approximately) by the requirement that the head–tail asymmetry of the interaction potential between two CO molecules vanishes when it is expanded about these “interaction centers.” Their positions on the molecular axes can be estimated by looking at the van der Waals bond length in (CO)\(_2\) dimers as a function of the orientations of the CO molecules (cf. Fig. 1 of Ref. 14).

FIG. 2. Phonon dispersion curves for \(\alpha\)-CO in the P\(2_{\overline{3}}\,3\) structure, calculated from the \textit{ab initio} potential in the spherical expansion.

FIG. 3. Phonon dispersion curves for \(\alpha\)-CO in the P\(2_{\overline{3}}\,3\) structure, calculated with the site–site model fit to the \textit{ab initio} potential.
must lie more toward the C atoms, while the center of mass lies closer to the O atoms. The effective \( P_{a3} \) symmetry observed by x-ray diffraction\(^4\) can then be explained by concluding (as supported semiquantitatively by our calculations) that the centers of electronic charge distribution of the CO molecules are situated on the centrosymmetric face-centered-cubic (fcc) sites of the \( P_{a3} \) lattice. Thus, the centers of mass will be displaced in the direction of the oxygen atoms. When a specific CO molecule makes a head–tail flip, simultaneously its center of mass moves over to the other side of the centrosymmetric lattice site. Since the molecular centers of interaction do not coincide with their centers of mass, there will be strong mixing between the librations and the translational vibrations. Such mixing is indeed observed and it leads, for instance, to the lowering of the lowest librational frequency (see Table IV).

Next we compare the calculated lattice frequencies with the measured Raman\(^18\) and infrared\(^19,20\) spectra. The values calculated directly from the \textit{ab initio} potential (in the spherical expansion) agree very well with the experimental data (see Table V). This applies primarily to the calculations on the \( P_{2,3} \) structure, but we find that the values obtained for the \( P_{3} \) structure (with one flipped CO molecule in the unit cell) are very similar. The assignment given in Table V is somewhat different from the original assignment of the Raman spectrum. Anderson et al.\(^16\) could not assign the shoulder which they observed at 38 cm\(^{-1}\); they believed that its occurrence was related to the orientational disorder. They based their assignment on empirical lattice dynamics calculations for pure librations in the \( P_{a3} \) structure which did not yield sufficiently low frequencies. We find, however, that the lowest librational mode is softened considerably (from 54.0 to 35.8 cm\(^{-1}\)) by the admixture of translational character. Moreover, we calculate that this mode retains nearly the same frequency in the \( P_{3} \) structure. So we think that the shoulder observed at 38 cm\(^{-1}\) actually corresponds to the lowest \( E \) mode. Our assignment of the lower modes also differs from that by Fracassi et al.\(^12,13\) The assignment in Table V is supported by the intensities. The peaks observed in the infrared spectrum (at 50.5 and 86 cm\(^{-1}\)) are ascribed to the infrared allowed \( T \) modes with the highest translational character (see Table IV); the pure translational \( A \) mode excitation is infrared forbidden in \( P_{2,3} \) symmetry. Raman excitations are allowed for all symmetries \( A, E, \) and \( T \). The strongest peaks in the Raman spectrum (at 44 and 90.5 cm\(^{-1}\)) are assigned to the modes with the largest librational components. All these assignments are somewhat uncertain, however, since the main peak observed in the Raman spectrum is very broad and the local symmetry is lower than \( P_{2,3} \) because of the random head–tail disorder.

The lattice frequencies calculated with the site–site model fit to the \textit{ab initio} potential are generally not very different, except for the highest, mainly librational mode at 119.1 cm\(^{-1}\), which is considerably too stiff. The LO–TO splittings calculated by the Ewald model are too small to be observed.

These authors observed a strong coupling between the librations and the transverse acoustic modes, which is reflected by an anomalous dispersion of these modes. Although we also observe this strong coupling which leads to the substantial lowering of the lowest optical (\( E \)-mode) frequency that is mentioned above, we do not observe an anomalous dispersion of the acoustic branches.

Summarizing this discussion, we arrive at the following conclusions: First, we observe that the \textit{ab initio} CO–CO potential, without any adjustment, yields a very realistic lattice structure and cohesion energy, as well as a set of lattice frequencies in good agreement with the spectroscopic values. Translation–rotation coupling appears to be important indeed. A different head–tail order of the CO molecules does not lead to large energetical differences, provided that the head–tail reversal of a molecule is accompanied by a translational shift to the opposite side of the centrosymmetric lattice site to which it belongs in the (average) \( P_{a3} \) structure. Also, the lattice frequencies are not strongly affected by head–tail reordering, but the relatively small shifts and splittings of all the individual frequencies may well explain the very broad peak observed in the Raman spectrum of the (disordered) \( \alpha \) phase.

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