Molecular Spectra and Molecular Symmetry of CO Dimer

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The transition selection rules, observed by millimeter wave spectroscopy, allow us to identify the symmetry of each ro-vibrational level uniquely. In this study the vibrational assignments have been established for the low-lying energy levels of the CO dimer on the basis of the molecular symmetry group (PI group).

I. Molecular symmetry group G_4

Assuming that the CO bond is strong enough, the feasible symmetry operations for CO dimer are the simultaneous permutation of identical nuclei P=(A,B)(1,2), inversion of the coordinates E*, and the product of the two P*=PE*, in addition to the identity operator E, where 1, 2, A, and B represent the nuclei as defined in Fig 1. Although C_{2h} symmetry is assumed in the figure, it should be emphasized that the molecular symmetry group based on the permutation-inversion (PI) operations does not require any special configuration. These four symmetry operations form a group, which is G_4: the character table of the irreducible representation is given in Table 1.

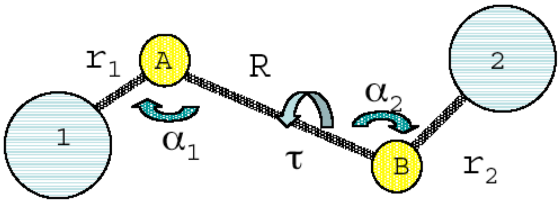

Fig. 1 A possible configuration of CO dimer is illustrated: A and B represent carbon atoms, and 1 and 2 oxygen atoms

II. Symmetry properties of the rotational wavefunctions

By inspecting the transformation properties of the molecular structure upon the symmetry operations, the *equivalent rotations* of the operations can be derived as R_y^{π} for P and E*, and R_y^{0} for E and P*.

We assume here that the molecule fixed z-axis is the axis connecting the centers of mass of the two CO molecules, and that the atoms 1, A, and B are on the xz-plane. The effect of the symmetry operations on the rotational wavefunctions are then given by the transformation properties for the *equivalent rotation*: $K_c = e$ is s+ and $K_c = o$ is a−. Here the I^r axis choice is applied which is appropriate for the CO dimer

Table 1
Symmetry Group G_4 and C_{2h}

C_{2h}		E	C_2	σ_h	***i***
	G_4	E	P	E*	P*
A_g	s+	1	1	1	1
B_u	a+	1	−1	1	−1
A_u	s−	1	1	−1	−1
B_g	a−	1	−1	−1	1

III. Symmetry properties of the vibrational wavefunctions

Table 2

Symmetry coordinates

ν_1:	$\Delta r_1+\Delta r_2$	: A_g (s+)
ν_5:	$\Delta r_1-\Delta r_2$	: B_u (a+)
ν_2:	ΔR	: A_g (s+)
ν_3:	$\Delta\alpha_1+\Delta\alpha_2$	: A_g (s+)
ν_6:	$\Delta\alpha_1-\Delta\alpha_2$	: B_u (a+)
ν_4:	$\Delta\tau$	: A_u (s–)

The vibrational coordinates, *i.e.* the displacements in the structure parameters defined in Fig. 1, can be symmetrized as listed in Table 2, together with the symmetry notations for C_{2h} and G_4. ν_1 and ν_5 are the symmetric and anti-symmetric CO stretching vibrations. The others are the cluster vibrations which are of interest in the present study.

IV. Vibrational assignments

The symmetry of the dipole moment is s–, and therefore the dipole transition selection rules are given for the ro-vibrational symmetry as s+ <––> s– and a+ <––> a– , which is expressed as the product of the rotational and vibrational symmetry. From the transition selection rules, and by careful consideration of all observed transitions, the symmetry and *K* assignments of the various levels have been determined and are given in Fig. 2.

Fig. 2 The observed energy levels are presented with the vibrational assignments made in the present study

[energy levels from Tang *et al*., J. Mol. Spectrosc. **214**, 87-93 (2002)].