

Combined Jahn–Teller and Pseudo-Jahn–Teller Effect in the CO₃ Molecule: A Seven-State Six-Mode Problem

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Abstract: A complicated problem of seven electronic states in four terms, $^1A_1'$, $^1E''$, $1^1E'$, and $2^1E'$, interacting with six vibrational modes, a_1' , a_2'' , e' , and e'' , was solved to take into account the combined two-mode Jahn–Teller (JT) plus two-mode pseudo JT effects and rationalize the electronic structure of the CO₃ molecule. The JT and first-order pseudo JT effects in the E'' state are separated from the rest of the problem by symmetry; they do not influence the ground state properties. In the remaining five-state five-mode problem including the ground state, $(A_1' + 1E' + 2E') \otimes (a_1' + e' + e'')$, the JT two-mode problem is reduced to the one-mode one by means of coordinate transformations. Several high-level ab initio calculations including all of the five states confirm the previously found coexistence of a central minimum of D_{3h} symmetry and three equivalent minima with a distorted geometry of C_{2v} symmetry in the ground state; the barrier between them is rather small, 0.2–0.3 eV, but large enough to distinguish them spectroscopically. Harmonic vibrational frequencies of the two configurations near the minima of the adiabatic potential energy surface are also evaluated. The calculations show how the distorted configurations are produced by the JT effect in one of the excited E states, similar to a previous finding in O₃. Numerical data of ab initio calculations yield also the effective vibronic and primary force constants for all of the terms. An electronic structure problem of this complexity including a reduction of the two-mode problem to one mode with full interpretation of the origin of coexisting different geometries as due to the JTE in the excited state is presented here for the first time.

Introduction

The carbon trioxide CO₃ molecule is of significant interest due to its potential role in the atmospheric chemistry of Earth and Mars.^{1–9} The necessity to characterize the CO₃ molecule emerged first from the data on the photolysis of ozone–carbon dioxide ices at 77 K.² Attention to this system was renewed recently by the studies of kinetics of the reaction of carbon dioxide CO₂ with oxygen.^{1–8} It was proved that CO₃ is an important intermediate in the quenching of the electronically excited oxygen atoms O(¹D) by CO₂ and the ¹⁸O isotope enrichment of stratospheric carbon dioxide. The O(¹D) atom is initially generated by the photolysis of stratospheric ozone; it then collides with CO₂ to form CO₃, followed by

dissociation to CO₂ and the O atom in the ground ³P or excited ¹D electronic state via oxygen quenching or an isotope exchange mechanism.

Quite a number of experimental and theoretical investigations have been devoted to the structure of the CO₃ molecule. Ung and Schiff¹⁰ in 1966 postulated the existence of the CO₃ species in the gas phase without its explicit detection. Later, Moll et al.² and Jacox and Milligan⁴ investigated the infrared spectrum and derived a planar C_{2v} structure at low temperatures. Earlier experiments predicted that CO₃ in the C_{2v} configuration is produced in the reaction of CO₂ + O(¹D).¹¹ The latest experimental exploration of the structure of CO₃ was carried out by Jamieson and co-workers in 2006.¹² It was the first spectroscopic detection and identification of the D_{3h} configuration of CO₃.

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In 1987, Van de Guchte et al.¹³ performed self-consistent field (SCF) calculations on CO₃ and predicted a stable D_{3h} structure with lower energy than in the C_{2v} geometry. This calculation is likely to be too simple to give a reliable conclusion, but it inspired further interest in elucidating the geometric and electronic structure of CO₃. Castro and Sylvio¹⁴ used many-body perturbation theory and couple-cluster calculations to confirm that the C_{2v} and D_{3h} isomers coexist, but the C_{2v} structure lies about 18 kJ/mol lower than the D_{3h} isomer.

In recent years, higher-level computational methods have been used extensively to explore the structure of the CO₃ molecule. In 2004, on the basis of the complete active space self-consistent field (CASSCF) optimized geometries and internal contracted multireference configuration interaction with Davidson's cluster correction (MRCI + Q) single-point energies, Mebel et al.¹⁵ and Bennett et al.⁸ predicted that the C_{2v} and D_{3h} configurations have similar energies (the energy difference is about 0.1 kcal/mol) and are separated by a transition state with a barrier of about 4.4 kcal/mol. In 2007, Kowalczyk and Krylov¹⁶ performed a series of coupled cluster calculations (CCSD, CCSD(T), CCSDT, EOM-CCSD, and EOM-EE(2,3)) to study the electronic structure of CO₃. They were the first to involve the influence of the excited state via the pseudo Jahn–Teller effect (JTE) in the formation of the ground state geometry of this molecule (for other systems, this procedure has been previously involved many times^{17,18}), but they took into account only one excited state in a one-mode treatment. In the calculations of this paper,¹⁶ the D_{3h} minimum disappears at higher levels of correlation treatment and basis set, and only the C_{2v} minimum remains. The authors explained the disappearance of the high-symmetry equilibrium configuration by pointing out that in previous multireference studies dynamical correlation was not included in the geometry optimization. More recently, Qin and Soo¹⁹ used the DFT method to support the conclusion of coexistence of the D_{3h} and C_{2v} geometries.

Despite these theoretical studies performed on CO₃, the main question of the ground state configuration and geometry, D_{3h} versus C_{2v} , as well as expected vibrational frequencies at the minima, remains controversial, and no full discussion of the origin of this complicated adiabatic potential energy surface (APES) is given. The presence of a C_{2v} minimum with a symmetry lower than the highest one, D_{3h} , in the nondegenerate ground state indicates that there is an essential implication of the JTE involving excited electronic states.^{17,18} This means that to rationalize the results of ab initio calculations one has to take into account the mixing of the ground and all relevant excited states via the JTE and pseudo JTE (PJTE), which seems to be crucial in this problem. In any full consideration of this system, the three close-in-energy excited E states, each of which is potentially subject to JTE and PJT mixing with the others and with the ground state via the six active vibrations, must be taken into account. This amounts to a combined JTE plus PJTE seven-state six-mode problem, which can be reduced by symmetry to three simpler problems, the main of which is the five-state five-mode one that includes the ground state. The present paper reports a solution of these problems which

rationalizes the electronic structure of CO₃ and gives a clear physical picture of the origin of its two coexisting configurations in the ground state.

Formally, the APES obtained in this paper may serve as a basis for evaluation of the full rovibronic spectrum of CO₃. This is a separate and very difficult problem; we do not know of any precedent rovibronic solutions of this complexity. Partial solutions were discussed by Stanton²⁰ for the radical NO₃, which looks similar to CO₃ but is essentially different.

The JTE and PJTE in CO₃

According to the one-point calculations of the CO₃ molecule in the high-symmetry configuration D_{3h} in this and previous works, its ground state is $^1A_1'$, and there are three spin-singlet excited electronic terms, E'' , $1E'$, and $2E'$, that we found located at about, respectively, $\Delta = 0.97$ eV, $\Delta_1 = 2.65$ eV, and $\Delta_2 = 2.81$ eV above the ground state, and six vibrational modes: totally symmetric a_1' , out-of-plane a_2'' , bend e' (denoted below as $1e'$), and CO stretch e' (denoted below as $2e'$). In principle, all of these electronic terms and vibrations are involved in the formation of the APES of this molecule and its properties.

The first simplification of the problem can be obtained based on the fact that the E'' term does not mix with the ground state A_1' (in first order of the displacements) as there are no e'' vibrations in CO₃, and it mixes with the higher excited $1E'$ and $2E'$ terms via the out-of-plane displacements a_2'' , which are not active in the remaining five-state five-mode problem. This allows us to separate the main combined $(A_1' + 1E' + 2E') \otimes (a_1' + 1e' + 2e')$ two-mode JT plus two-mode PJT problem¹⁷ from the pure excited state JT $E'' \otimes (a_1' + 1e' + 2e')$ and PJT $(E'' + 1E' + 2E') \otimes a_2''$ problems. The vibronic coupling effects in the latter two problems are rather weak and not significant (see below).

The 5×5 secular matrix of the main problem contains a large number of constants including the JT vibronic coupling constants of each of the electronic terms to each of the vibrations and the PJT coupling constants between them, as well as the primary force constants and quadratic coupling constants. Fortunately, the problem can be simplified employing the results of the general theory of the multimode JTE (see in ref 17, sections 3.5 and 5.5; ref 21, and ref 22, as well as ref 23). According to the theory, the JT two-mode problem can be reduced to the ideal (one-mode) one by means of transformations in the coordinate system. In the transformed coordinates, only one e mode is JT-active (the *interaction mode*), the other one remaining non-JT-active (meaning harmonic and nonshifted), so the problem becomes $(A_1' + 1E' + 2E') \otimes (a_1' + e')$, and the JT plus PJT secular matrix is considerably simplified. The interaction mode stands for the total distortion produced by the nuclear displacements in the two modes, which in an appropriately chosen coordinate system is described by one minimum of the APES. Although the interaction mode is a function of the initial modes, and the reduced number of vibronic coupling constants is a combination of the larger number of initial constants, the problem is still essentially simplified because, as shown below, the interaction mode can be obtained from the ab initio calculations.

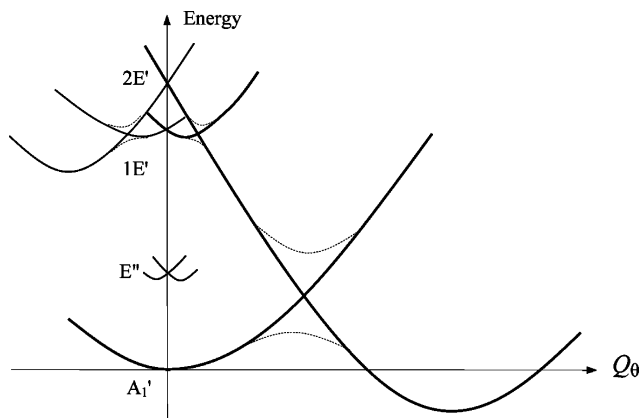


Figure 1. Schematic diagram of energy level of the ground state A_1' and four excited state ($1E'$ and $2E'$ in D_{3h} symmetry) dependence on the Q_θ coordinate of the interaction mode when their PJT mixing is ignored ($F_{ij} = 0$). The order of magnitude of the JT vibronic coupling constants is taken approximately in accordance with the ab initio calculations.

To get preliminary qualitative hints on where to find the interaction mode and what should be expected from the numerical calculations, some initial estimates based on the general theory¹⁷ and previous experience¹⁸ may be useful. In particular, if we ignore the PJT interaction between the three terms and take the JT coupling constants approximately as they appear in the ab initio calculations, we obtain for the cross section $Q_\epsilon = 0$ the energy level dependence on Q_θ shown in Figure 1. In fact, to get this picture qualitatively, we should assume that the JTE in at least one of the excited E states is sufficiently strong so that the JT stabilization energy is larger than the energy gap to the ground state. This is just the picture we got in solving the problem of O_3 .¹⁸

In Figure 1, the JTE splitting in the two excited E states and the harmonic curve of the ground state are shown. We know qualitatively how these curves change when the PJTE interaction is included; it is indicated by the dashed lines. An important feature in this energy level scheme is that the JTE in the excited state strongly influences the ground state APES, resulting, as shown in the ab initio calculations below, in the formation of an additional minimum with lower (C_{2v}) symmetry. There are three equivalent directions of the JTE distortions in the (Q_θ, Q_ϵ) space, and hence, if an additional C_{2v} minimum is formed under the influence of the excited state, there will be two more of them, forming three additional equivalent minima in the space of the interaction mode.

Following the qualitative picture of Figure 1 (which is confirmed below by the ab initio calculations), we see that the direction from the central minimum (if any) to the distorted configuration C_{2v} is determined by the direction of the JT distortion in the excited E states, more precisely, in the direction of the combined two-mode (interaction mode) distortion plus a possible shift of the a_1' displacements. To have an idea how the interaction mode depends on the initial modes, consider first the $2E'$ term with the strongest JTE, the $2E' \otimes (1e' + 2e' + a_1')$ problem, which generally produces two kind of distortions, one of which is given in symmetrized displacements $(q_{1\theta}, q_{1\epsilon}, q_a)$ of the $1e'$ mode, the other in the coordinates $(q_{2\theta}, q_{2\epsilon}, q_a)$ of the second mode $2e'$. Obviously, the real displacements of individual atoms

are some vector sums of their displacements in each of these modes. The three modes have different frequencies.

The process of reducing the two-mode problem to a one-mode one is to perform first a scale transformation, $(q_i')^2 = K_i q_i^2$, that makes the elastic term isotropic (with the same force constant $K = 1$ for all q_i' coordinates)²² and then an orthogonal transformation (rotation) for $q_{i\theta}'$ and $q_{i\epsilon}'$ and a shift for q_a' of the coordinate systems $(q_{i\theta}', q_{i\epsilon}', q_a')$ to new ones $(Q_{i\theta}, Q_{i\epsilon}, Q_a)$ in such a way that one of the modes becomes JT-inactive (has no linear terms in the Hamiltonian), the other one being accordingly modified. The transformation of the two-mode problem to a one-mode one with quadratic terms included was carried out recently by Polinger²³ (in previous works, only linear displacements were taken into account). In this transformation, the coupling to the totally symmetric coordinates can be separated by means of a shift along the Q_a axis. Performing the 2×2 transformation in the remaining (Q_θ, Q_ϵ) space, we get

$$\begin{aligned} Q_\theta &= c_1 q_{1\theta} + c_2 q_{2\theta} \\ Q_\epsilon &= d_1 q_{1\epsilon} + d_2 q_{2\epsilon} \end{aligned} \quad (1)$$

where the coefficients of this transformation are combinations of linear and quadratic vibronic coupling constants and force constants of all three modes.²³ Their exact numerical evaluation is not the goal of our calculation, but in further exploration of the excited states, this may be necessary. The main role of the interaction mode is to allow us to reformulate the problem in terms of $(A_1' + 1E' + 2E') \otimes (a_1' + e')$ with one e mode instead of two and to determine the effective JT parameters of this interaction mode (meaning the parameters of the APES of the excited state) by comparison with the numerical data. Numerically, the constants in eq 1 will also be affected by the influence of the JTE on the $1E'$ term, but this influence is insignificant. The JTE on this term, as shown in the calculations below, is very small, and the contribution of its quadratic terms (which only contribute to the warping of the Mexican hat) is negligible (anyhow, it just changes the expressions for the coefficients in eq 1).

For the direction from the D_{3h} minimum to the expected C_{2v} minimum which coincides with the similar direction to the corresponding minimum of the JTE $2E' \otimes (a_1' + e')$ in the excited $2E'$ term (Figure 1), we should take into account that the minimum on the Q_θ axis (where $Q_\epsilon = 0$) has also a shift component along the Q_a axis. This follows directly from the general solution of the quadratic $E \otimes (a_1' + e')$ problem¹⁷ and is confirmed below in the ab initio calculations of the APES along the Q_a coordinate (see Figure 7). Therefore, in the space of the interaction mode, the direction from D_{3h} to C_{2v} to be matched with the numerical calculations below is

$$Q_\theta = c_1 q_{1\theta} + c_2 q_{2\theta} + c q_a \quad (2)$$

With only one active e' mode taken into account and in the space of its coordinates, we can write the effective matrix equation for the potential energy of the system (the APES) of the $(A_1' + 1E' + 2E') \otimes (a_1' + e')$ problem as follows (\mathbf{I} is a unit matrix 5×5):

$$\mathbf{W} - \mathbf{EI} = 0 \quad (3)$$

where

$$W = \begin{bmatrix} W_1 & F_{12}Q_\theta & F_{12}Q_\varepsilon & F_{13}Q_\theta & F_{13}Q_\varepsilon \\ F_{12}Q_\theta & W_2 - F_{22}Q_\theta + N_{22} + F_2^a Q_a + F_2^{ae} Q_a Q_\theta + \Delta_1 & F_{22}Q_\varepsilon + 2G_{22}Q_\varepsilon Q_\theta + F_2^{ae} Q_a Q_\varepsilon & F_{23}Q_\theta + F_{23}^a Q_a & F_{23}Q_\varepsilon \\ F_{12}Q_\varepsilon & F_{22}Q_\varepsilon + 2G_{22}Q_\varepsilon Q_\theta + F_2^{ae} Q_a Q_\varepsilon & W_2 + F_{22}Q_\theta - N_{22} + F_2^a Q_a - F_2^{ae} Q_a Q_\theta + \Delta_1 & F_{23}Q_\varepsilon & F_{23}Q_\theta + F_{23}^a Q_a \\ F_{13}Q_\theta & F_{23}Q_\theta + F_{23}^a Q_a & F_{23}Q_\varepsilon & W_3 - F_{33}Q_\theta + N_{33} + F_3^a Q_a + F_3^{ae} Q_a Q_\theta + \Delta_2 & F_{33}Q_\varepsilon + 2G_{33}Q_\varepsilon Q_\theta + F_3^{ae} Q_a Q_\varepsilon \\ F_{13}Q_\varepsilon & F_{23}Q_\varepsilon & F_{23}Q_\theta + F_{23}^a Q_a & F_{33}Q_\varepsilon + 2G_{33}Q_\varepsilon Q_\theta + F_3^{ae} Q_a Q_\varepsilon & W_3 + F_{33}Q_\theta - N_{33} + F_3^a Q_a - F_3^{ae} Q_a Q_\theta + \Delta_2 \end{bmatrix}$$

In the formation of this equation, the wave functions of the two E_i terms are denoted by $li\theta\rangle$ and $li\varepsilon\rangle$, $i = 2$ and 3 , and that of the ground state is $la\rangle$. The 5×5 secular matrix (eq 3) contains the effective constants of vibronic coupling to e' displacements, with linear F_{ii} ($i = 2, 3$) and quadratic G_{ii} ($i = 2, 3$), and three constants F_{ij} ($ij = 12, 13$, and 23) of pseudo JT coupling between the terms by e' displacements, as well as the diagonal quadratic coupling terms $N_{ii} = G_{ii}(Q_\theta^2 - Q_\varepsilon^2)$ and elastic energies $W_i = (1/2)K_i(Q_\theta^2 + Q_\varepsilon^2) + (1/2)K_i^a Q_a^2$, $i = 1-3$, and the constants of the vibronic coupling of the three electronic terms to Q_a displacements F_i^a ($i = 2, 3$) and one constant F_{23}^a of the coupling between the two E terms. The F_i^{ae} ($i = 2, 3$) are the quadratic constants for interactions between the a_1' and e' modes.

We emphasize that because of the transformations above the relation between these constants and the initial JT constants of coupling to the two e' modes are complicated and in fact unnecessary, as the latter are unobservable. The APES matrix (eq 3) should be regarded as the *effective potential energy matrix*, which describes the real surface to be obtained in the ab initio calculations below. The parameters in this matrix are thus *effective* coupling constants that describe the APES. Some of these constants are not directly related to observable properties (e.g., the primary force constants K_i for JT modes¹⁷). The derivations and discussion above show how the real APES is formed by complicated JT interactions between the electronic states and vibrational modes in the D_{3h} configuration, especially, why we can consider only one JT vibrational mode instead of two. After accepting this conclusion, we can ignore eqs 1 and 2 and start further consideration from eq 3.

As mentioned above, the electronic structure of CO_3 is somewhat similar to that in the ozone molecule O_3 where the three minima of the obtuse triangular (C_{2v}) configuration are formed under the strong influence of the JTE in the excited E state,¹⁸ and there is a shallower minimum with the D_{3h} configuration. But compared with O_3 , the CO_3 molecule is much more complicated because of the two-mode problem and the presence of three excited close-in-energy E terms in the high-symmetry configuration, with two of them strongly influencing the ground state. Among four-atomic molecules, CO_3 is the most complicated system studied in this respect.

Ab Initio Calculations

In all of the ab initio calculations for this problem, Dunning's correlation consistent basis set cc-pVTZ²⁴ is employed. The active space is composed of the extensively used 16 electrons and 13 active orbitals (i.e., all valence electrons and orbitals with the exception of 2s lone pairs of oxygen atoms) denoted as (16/13). Another smaller active space is (16/10), which excludes the three empty orbitals corresponding to the three antibonding σ_{CO}^* 's based on (16/13). The inactive orbitals (1s of C and 1s and 2s of O) were kept frozen temporarily only when the smaller active space (16/10) was used.

The geometry optimizations and frequency calculations were performed by single-state CASSCF (SS-CASSCF)²⁵ and MRCI+Q methods²⁶ (Tables 1 and 2). In addition, state-average CASSCF (SA-CASSCF)²⁷ calculations were carried out to optimize the stationary points and scan the potential energy curves. On the basis of the SS-CASSCF or SA-CASSCF geometry, the MRCI+Q single-point energies are also obtained to account for the dynamical correlation. Considering the computational efficiency, only reference configurations with weights larger than 1×10^{-4} were selected to be correlated in the MRCI+Q calculations with 16/13 active space.

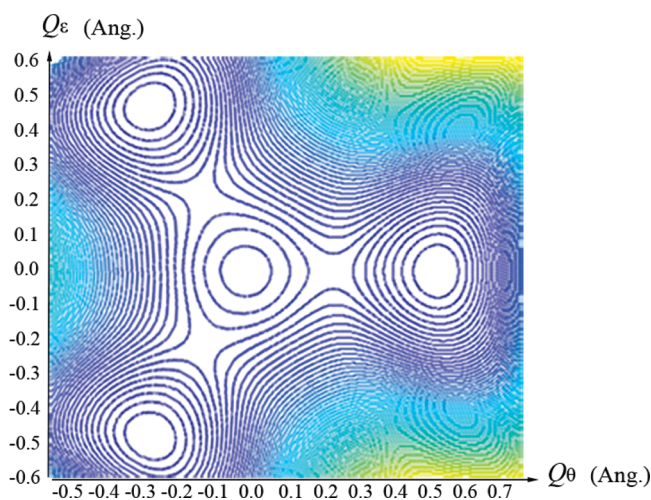
Besides the multireference methods above, two high-level single-reference methods, that is, Brueckner coupled-cluster doubles with perturbative triples (BCCD(T))²⁸ and coupled-cluster involving singles and doubles with perturbative triples and quadruples (CCSD(TQ)),²⁹ were used to optimize the structures and calculate the frequencies at the minima.

Table 1. Optimized Geometries (Bond Lengths in Ångstroms and Angles in Degrees), Energy Differences ΔE (in eV), and Total Energies (in au) at the D_{3h} Minimum of the CO_3 Molecule Obtained by Different Computational Methods

methods	D_{3h} , $R(\text{CO})$	C_{2v}			$\Delta E (E_{C_{2v}} - E_{D_{3h}})$	total energy (D_{3h})
		$R(\text{CO}^1)$	$R(\text{CO}^2)$	$\angle \text{O}^1 \text{CO}^2$		
MRCI+Q (16/10)	1.2550	1.1718	1.3252	142.2	−0.11	−263.27351667
MRCI+Q//SS-CASSCF(16/13)	1.2637	1.1739	1.3380	142.1	−0.10	−263.28928534
MRCI+Q//SA-CASSCF(16/13)	1.2635	1.1727	1.3428	142.2	−0.08	−263.28907391
BCCD(T)	1.2597	1.1758	1.3333	142.6	−0.23	−263.29442881
CCSD(TQ)	1.2570	1.1745	1.3324	142.4	−0.28	−263.29093183

Table 2. Frequencies of CO₃ in cm⁻¹ at the Minima Obtained with Different Methods

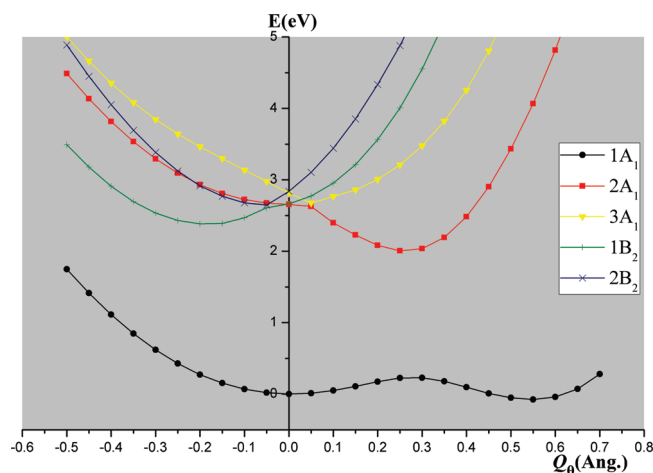
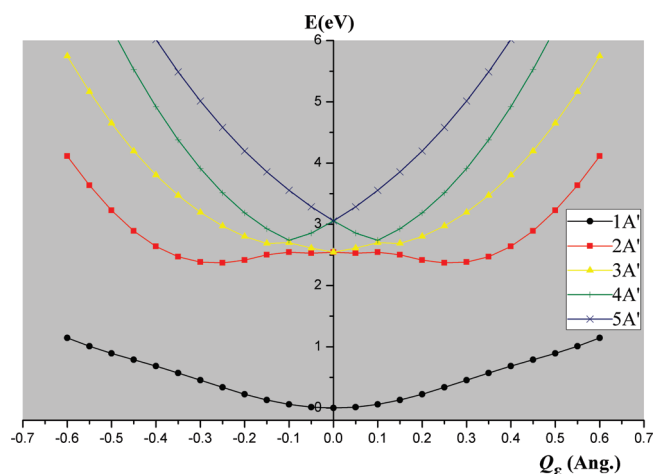
mode (symmetry)/methods	MRCI+Q (16/10)	SS-CASSCF(16/13)	BCCD(T)	CCSD(TQ)	CCSD(T) ^a
<i>D</i> _{3h}					
bend (<i>e'</i>)	460	440	455	466	-402
OPLA (<i>a</i> ₂ '')	769	761	762	772	776
CO stretch (<i>a</i> ₁ '')	1124	1084	1094	1113	1105
CO stretch (<i>e'</i>)	1647	1182	1316	1274	1093
<i>C</i> _{2v}					
bend (<i>b</i> ₂)	591	580	567	575	575
bend (<i>a</i> ₁)	604	578	612	597	606
OPLA (<i>b</i> ₁)	694	682	672	675	683
CO stretch (<i>b</i> ₂)	1049	1017	1006	1017	1007
OCO stretch (<i>a</i> ₁)	1122	1075	1093	1096	1099
CO stretch (<i>a</i> ₁)	2100	2071	2066	2073	2078

^a Ref 16.**Figure 2.** Equipotential curves on the APES of the ground state of CO₃ in the cross section of the (*Q*_θ, *Q*_ε) plane of the interaction mode obtained by the BCCD(T) method.

All of the calculations were performed using the MOLPRO quantum chemistry program package,³⁰ except the CCSD(TQ) calculations performed with the ACES II program.³¹

Energies and Optimized Geometries of CO₃

Figure 2 shows the equipotential curves on the contour map of the APES of the ground state of CO₃ in the cross-section of the (*Q*_θ, *Q*_ε) plane of the interaction mode obtained by the BCCD(T) method (SA-CASSCF yields a similar surface, which is not shown here). Figures 3 and 4 present the energy levels of all three terms (*A*₁'', 1*E*', and 2*E*') in the cross-section of the APES along the two interaction coordinates *Q*_θ and *Q*_ε, respectively. The CO₃ geometries in the *D*_{3h} and *C*_{2v} configurations of the APES minima are shown in Figure 5. Figure 6 shows the energy levels of all four terms (*A*₁', *E*'', 1*E*', and 2*E*') as a function of the out-of-plane *a*₂'' displacement. They all remain approximately harmonic, so there are no significant implications caused by the separation of the (*E*' + 1*E*' + 2*E*') ⊗ *a*₂'' problem. The PJTE here is weak, lowering the corresponding vibrational frequencies but not producing instabilities (see the weak PJTE¹⁷). Similarly, the mixing of the three terms *A*₁', 1*E*', and 2*E*' under totally symmetric displacements, as seen from Figure 7, is also weak, but the two excited states have shifted minimum positions in accordance with eq 4 obtained below. Numerical

**Figure 3.** Ground 1*A*₁ and four excited state energy levels (2*A*₁ and 1*B*₂ and also 3*A*₁ and 2*B*₂ correspond to 1*E*' and 2*E*' in *D*_{3h} symmetry, respectively) of CO₃ in the cross-section of the APES along the interaction mode *Q*_θ obtained by the MRCI+Q//SA-CASSCF (16/13) method.**Figure 4.** Ground 1*A*' and four excited energy levels (2*A*' and 3*A*' and also 4*A*' and 5*A*' correspond to 1*E*' and 2*E*' states in *D*_{3h} symmetry, respectively) of CO₃ in the cross-section of the APES along the interaction mode *Q*_ε obtained by the SA-CASSCF (16/13) method.

data, on geometries, energies, and frequencies of CO₃ calculated by different computational methods, are listed in Tables 1 and 2.

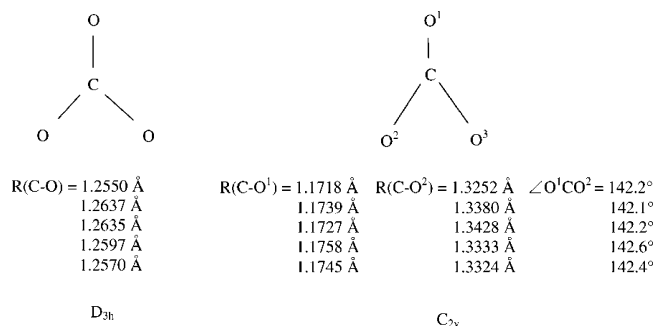


Figure 5. Optimized CO_3 geometries of the D_{3h} and C_{2v} configurations at the APES minima (bond lengths in Å and angle in degrees) obtained by MRCI+Q(16/10), SS-CASSCF(16/13), SA-CASSCF(16/13), BCCD(T), and CCSD(TQ) methods, respectively.

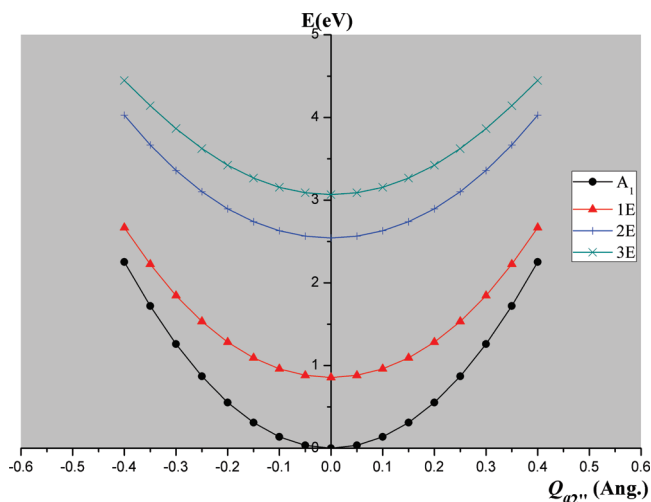


Figure 6. Energy levels of all four terms (A_1' , E'' , $1E'$, and $2E'$ states corresponding to the A_1' , E'' , $1E'$, and $2E'$ states in the D_{3h} point group) along the out-of-plane $Q_{a2''}$ displacement calculated with the SA-CASSCF(16/13) method.

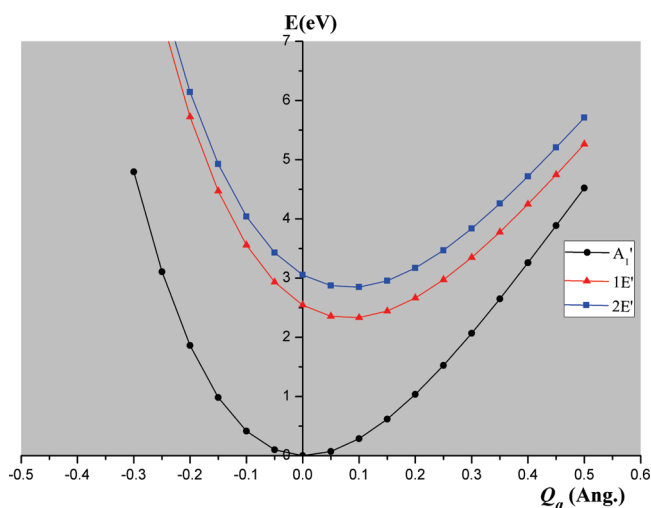


Figure 7. Energy levels of the three terms (A_1' , $1E'$, and $2E'$) along the totally symmetric displacements Q_a calculated with the SA-CASSCF(16/13) method.

All of the methods used in the present study reveal two kinds of minima in the ground state APES of CO_3 : the central minimum, which yields the geometrical structure of D_{3h}

symmetry, and three equivalent minima of C_{2v} symmetry. The latter have slightly lower energy than the D_{3h} minima. The single-reference methods, BCCD(T) and CCSD(TQ), produce much larger energy differences between the two minima than the multireference methods (Table 1). We also found that the results of MRCI+Q with the active space of (16/10) are similar to those of the SS-CASSCF and SA-CASSCF methods obtained with the more time-consuming (16/13) active space. It shows that, for the system under consideration, the dynamical correlation may strongly influence the relative energies but affect less the optimized geometry and frequencies.

In addition to the dominant closed-shell configuration $(4a_1')^2(1a_2'')^2(3e')^4(4e')^4(1e'')^4$ in the active space with a weight of 69%, SA-CASSCF calculation shows that there is a two-electron excited configuration $(4a_1')^2(1a_2'')^2(3e')^4(1e'')^4(4e')^2(1a_2')^2$ with a weight of 18% in the ground state, which means the single-reference method may fail. To remedy this, higher-order correlations should be included. In one of the previous papers,¹⁶ the D_{3h} minimum was not found in the calculations by CCSD and CCSD(T) methods. Their total energies, geometries, and frequencies could not be exactly reproduced in our calculations, and the discrepancy cannot be explained by a numerical error. The results that we obtained for this case with different programs agree very well (the D_{3h} configuration was checked at different levels by ACES II,³¹ MOLPRO,³⁰ and several other quantum chemistry programs). Arguably, this discrepancy may be caused by the defects in the HF-SCF codes of the old version of ACES-II. In our computations with the BCCD(T) and CCSD(TQ) methods, we got the D_{3h} minimum, quite similar to the results of the MRCI+Q method.

For the excited states of CO_3 , SA-CASSCF (16/13) calculations also show that there is a large static correlation contribution. In particular, for the $2E'$ state, the dominant electronic configuration comes from a two-electron excitation of the ground state, which cannot be described well by single-reference methods, such as popular EOM-CC and TDDFT. The multireference treatment is necessary in such cases. Perhaps this is the reason that in our multireference calculations of the excited states the energies are lower than those obtained by other methods (e.g., in ref 16).

Further Discussion: Jahn–Teller Parameter Values

As discussed above, it is seen in Figure 1 that the Q_θ coordinate of the interaction mode coincides with the line that connects the D_{3h} and C_{2v} minima. On the other hand, we can get the coordinate of this line from the ab initio calculations following the distortions from the geometry at the D_{3h} to the C_{2v} minima in terms of the symmetrized normal displacements a_1' , $1e'$, and $2e'$ in the D_{3h} geometry. This can be done by optimizing the corresponding linear combination of these coordinates to fit the numerical values of the atomic coordinates of CO_3 in the two minima. It yields (cf. eq 2) the following:

$$Q_\theta = 0.98931q_{1\theta} + 0.00479q_{2\theta} + 0.14574q_a \quad (4)$$

Similarly,

$$Q_e = 0.99999q_{1e} + 0.00485q_{2e} \quad (5)$$

The coefficients in the linear combination show that, in the distortion from the high-symmetry D_{3h} configuration to the C_{2v} one along the interaction mode, the contribution of the bend $1e'$ mode is overwhelming, and there is also a significant contribution from the totally symmetric displacements Q_a , which is understandable in view of the change in the average interatomic distances in this transformation. It is reflected also in the shift of the minimum along the Q_a coordinate in the excited E terms in Figure 7.

Comparing the computed energy levels of the five states (Figure 3) with those in Figure 1, we see that qualitatively the formation of the low-symmetry C_{2v} minima is indeed controlled by the JTE in the excited E states, similar to the O_3 case.¹⁸ But compared to the latter, the CO_3 system has a more complicated electronic structure. First, there are three excited state conical intersections in the D_{3h} symmetry of CO_3 and a considerable PJT interaction between two of the excited states at the avoided crossing point $Q_\theta = 0.05$ Å. More important is the interaction between the E_θ branch of the excited E state with the ground state at another point of avoided crossing ($Q_\theta = 0.30$ Å) that is very strong and produces a gap of $\Delta = 1.78$ eV between them (in O_3 , this interaction is very small). For this reason, the barrier between the two geometries, $\delta = 0.22$ eV, is much smaller than in O_3 , but it is still significantly higher than the zero vibration level, so the two configurations can be observed spectroscopically. The large energy gap at the avoided crossing may also quench the otherwise important topological (Berry) phase implications, which influence the rovibronic spectrum in the JT minima (see, e.g., the discussion of the O_3 case¹⁸).

On the contour map of the ground state APES in the space (Q_θ , Q_e) (Figure 2), the positions and the relative barriers between the central minimum and the peripheral ones and between any two C_{2v} minima are qualitatively different from many other multim minima APES in JT systems with ground state degeneracy.¹⁷ Indeed, while in the latter cases the transition between the peripheral minima goes directly between them sidestepping (bypassing) the high-symmetry configuration, in CO_3 , the direct barrier between the C_{2v} minima is very high as compared with the barrier to the D_{3h} one. This situation may be important in evaluation of the tunneling splitting, as well as the whole rovibronic spectrum.

The numerical results of the ab initio calculations allow us also to approximately estimate the values of the majority of the effective JT parameters in eq 3. To do this, we can produce further appropriate cross-sections of the multidimensional five-branched APES and compare the energies as functions of the JT parameters with ab initio obtained values. By fitting the ab initio data at small deviations from the D_{3h} symmetry with the roots of eq 3 in the cross-section $Q_e = 0$ with $Q_a = 0$, and $Q_\theta = 0$ with $Q_e = 0$, respectively the approximately estimated parameters are as follows: $K_1 = 18.92$ eV/Å², $K_2 = 30.40$ eV/Å², $K_3 = 14.17$ eV/Å², $F_{12} = 0.84$ eV/Å, $F_{13} = 2.99$ eV/Å, $F_{23} = 0.76$ eV/Å, $F_{22} = 0.73$ eV/Å, $F_{33} = 4.76$ eV/Å, $G_{22} = -4.34$ eV/Å², and $G_{33} = -5.70$ eV/Å²; $K_1^a = 70.95$ eV/Å², $K_2^a = 80.90$ eV/Å², $K_3^a = 78.58$

eV/Å², $F_2^a = 6.50$ eV/Å, $F_3^a = 6.32$ eV/Å, and $F_{23}^a \approx 0$. The fitting is approximate and may not be acceptable for large deviations from the D_{3h} symmetry. As expected (Figure 1), the strongest PJTE comes from the interaction between the ground state and the $2E'$ state, and the stronger JTE is in the degenerate $2E'$ state too. Even though the interaction between the other excited $1E'$ and the ground state A_1' is small, it cannot be ignored, as it affects indirectly the ground state structure through its JT and PJT interaction with the $2E'$ term. In total, the coexistence of the D_{3h} and C_{2v} equilibrium configurations in CO_3 is controlled by the combination of the JTE and PJTE, which mix five electronic states with five vibrational modes. The small F_i^{ae} constants of quadratic interactions between the a_1' and e' modes could not be obtained in our calculations because they fall out from the cross-sections of either $Q_a = 0$ or $Q_e = 0$, while calculation of the whole $Q_a Q_e$ surface is extremely time-consuming and seems to be excessive.

As for the separate excited state $E'' \otimes (a_1' + 1e' + 2e')$ problem, the calculations reveal a somewhat different interaction mode along which the JTE is very weak with a distortion (the radius at the bottom of the trough of the APES¹⁷) of $\rho_0 \approx 0.07$ Å, which hardly influences the geometry in this state.

Conclusion

The CO_3 molecule proved to have a very complicated electronic structure and two different, coexisting geometry configurations. An electronic structure problem of this complexity with a full explanation of the origin of peculiar geometries due to the JTE and PJTE in excited states is given here for the first time. High-level ab initio calculations of the APES of the ground and six (three two-fold degenerate in the high-symmetry configuration) excited electronic states in the space of all six (two two-fold degenerate in-plane, one totally symmetric, and one out-of-plane) active vibrational modes of the CO_3 molecule were performed and rationalized in terms of a combined two-mode JT and two-mode PJT problem. One excited state plus the out-of-plane mode were separated by symmetry. The two-mode JT problem was reduced to the one-mode one by means of a coordinate transformation. The coexistence of two types of APES minima with D_{3h} symmetry (one minimum) and C_{2v} symmetry (three equivalent minima) was confirmed, and the origin of the distorted configuration as due to the strong JTE in one of the excited states was revealed. The harmonic vibrational frequencies in the minima of the two configurations were also evaluated. The efficiency of the JTE theory in rationalizing the results of ab initio calculations is demonstrated here by the solution of a very complicated problem of CO_3 .

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