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Potential energy surfaces and Jahn-Teller effect on $CH_4\cdots NO$ complexes

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The potential energy surface of the $CH_4\cdots NO$ van der Waals complexes was explored at the RCCSD(T)/aug-cc-pVTZ level including the full counterpoise correction to the basis set superposition error. The Jahn-Teller distortion of the C_{3v} configurations for the CH bonded and CH_3 face complexes was analyzed. From this distortion, two A' and A'' adiabatic surfaces were considered. The estimated zero point energy of C_s configurations is above the barrier of the C_{3v} ones. Therefore, the CH_3 face complexes are dynamic Jahn-Teller systems. The D_0 (140 cm^{-1} for A'' state and 100 cm^{-1} for A') values obtained are in good agreement with the experimental values (103 ± 2 cm^{-1}) recently reported. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2752805]

I. INTRODUCTION

Historically, most of the work on van der Waals interactions and complexes was done for systems containing only closed-shell species. However, open-shell complexes may exhibit interactions that are intermediate between van der Waals and chemical bonding.[1] Recently, more attention, both experimental and theoretical, has been given to the study of systems containing open-shell species.[2] Complexes of open-shell species are expected to play an important role in chemical reactions in the atmosphere, in interstellar cloud collisions, ultracold molecules, and Bose-Einstein condensates. The interactions in these complexes are weak and strongly anisotropic and involve more than one electronic state.

Nitric oxide (NO) is one of the most important benchmark systems to study van der Waals interactions of open-shell molecules.[2] There are a significant number of investigations regarding the nature and spectroscopy of complexes between NO and rare gases.[2–5] For this purpose, resonance enhanced multiphoton ionization (REMPI) spectroscopy, matrix isolation, and *ab initio* calculations have been used frequently. There are some reports related with the interaction of NO with distinct molecules, e.g., N_2, CO, H_2O, CH_4, and C_2H_6.[5–15]

The complexes between NO and CH_4 have deserved great interest.[5,6,11–13,15] The first report, which appeared in 1987, was a comparative study of the X–NO complexes (X=Kr, Xe, CH_4) using multiphoton spectroscopy via the $\tilde{C}\leftarrow\tilde{X}$ transition.[5] Afterwards, Akiike *et al.* published a report on the $\tilde{A}\leftarrow\tilde{X}$ transition.[6] Wright and co-workers have studied these complexes employing REMPI spectra and *ab initio* calculations for the interpretation of the results.[11,12] They identified two kinds of complexes with *ab initio* calculations: The CH_3 face and the CH bonded ones. The CH_3 face complexes of C_s symmetries are the most stable at the $\tilde{X}$ state.[11] Recently, they studied extensively the $\tilde{A}\leftarrow\tilde{X}$ transition in isotopomers of $CH_4\cdots NO$ complexes.[12] Due to the complexity of the involved system, the interpretations of these spectra are not straightforward. There are no spectral lines related with the end-over-end rotation of the $CH_4\cdots NO$ complex and the spacings associated with rotational constant of the $^2A'$ state for the C_s complex are not observed. Therefore, the motion of NO is consistent with an effective C_{3v} symmetry in both electronic states (i.e., $\tilde{X}$ and $\tilde{A}$). Assuming effective C_{3v} geometries in both states, the authors can explain the observed REMPI spectra.

Whether this system is either a dynamic Jahn-Teller (JT) complex in which the A' and A'' components have zero-point vibrational energies (ZPEs) lying above the barrier or rather other phenomena are acting is not clear. It was particularly interesting that the spacings between the main features of the spectra are unaffected by isotopic substitution. According to calculations at MP2/aug-cc-pVTZ level, only the NO bending mode is unaffected by isotopic substitution. Hence, the REMPI spectra of $CH_4\cdots NO$ complexes were associated with a progression of the NO bending mode.[12]

Recently, the binding energy of the $CH_4\cdots NO$ complex was determined to be 198 ± 2 and 103 ± 2 cm^{-1} in $\tilde{A}$ and $\tilde{X}$ states, respectively, by velocity map imaging.[15] These values are similar to those reported by Musgrave *et al.*[12] (201.5 and 106.4 cm^{-1} for each state).

The aim of this work is to explore the potential energy surface (PES) at a high level of calculation including full counterpoise (CP) correction to basis set superposition error (BSSE) of $CH_4\cdots NO$ complexes in order to shed light about the JT effect in these complexes and to contribute to the interpretation of REMPI spectra.

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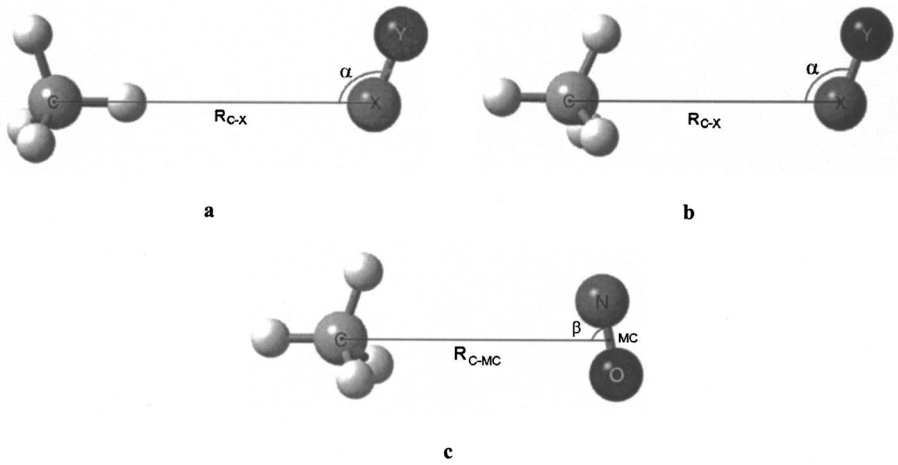


FIG. 1. Three calculated orientations (a, b, and c) for $CH_4\cdots NO$ complexes. X and Y are either N or O according to NO orientation.

II. COMPUTATIONAL DETAILS

For an accurate representation of these complexes and their PES's, a method that takes into account a considerable amount of electron correlation and a flexible basis set is needed. Moreover, the BSSE must be considered. Our previous work, regarding the effect of BSSE in the calculation of CH bonded C_{3v} complexes, shows the significant influence of this error in the PES's shapes.[13] The BSSE was corrected with CP procedure proposed by Boys and Bernardi.[16] The correct electronic state was employed for each fragment in these calculations; the radical fragment had in each case the symmetry of the complex (A' or A''). All energies and the cuts of PES's shown are the CP corrected and the geometries were obtained in these surfaces. Calculations of PES's were carried out employing RCCSD(T) (Ref. 17) method and the aug-cc-pVTZ (Ref. 18) Dunning's basis set. RCCSD(T) was used rather than UCCSD(T) in order to eliminate spin contamination.

An exploration over the whole surface is a difficult task, since there are many variables to change and the calculations can be very time demanding. Taking into account the suggestions made in previous experimental work,[12] it is possible to consider a small number of variables and obtain valuable information regarding the shape of PESs. In order to explore these complexes three orientations of NO around CH_4 molecule, shown in Fig. 1, were chosen. For the calculations, the CH_4 and NO geometrical parameters were fixed in their experimental values: $r(\mathrm{C-H})=1.094$ Å, $(\mathrm{H-C-H})=109.471°$, and $r(\mathrm{N-O})=1.151$ Å.[19] Orientations a and b (each one corresponds to a couple of NO positions: N orientated and O orientated) were used to explore the behavior of interaction energy with respect the α angle and the intermolecular distance $R_{\mathrm{C-X}}$ [see Figs. 1(a) and 1(b)]. The orientation c was employed to explore the PES of the CH_3 face complexes, as a function of the β angle and the intermolecular distance from C atom of methane to the mass center of NO, $R_{\mathrm{C-MC}}$ [see Fig. 1(c)]. These complexes are the most stable according to the results obtained with orientations a and b and the previous reports.[11] All calculations were carried out using MOLPRO suite of programs.[20]

The optimization of the three orientations a, b, and c leads to eight molecular configurations, which are denominated and collected in Fig. 2. Four CH_3 face complexes (X_G) present two C_{3v} complexes ($\mathrm{N}_{C_{3v}}$ and $\mathrm{O}_{C_{3v}}$) and two C_s complexes (N_{C_s} and O_{C_s}), X being the atom of NO that is closer to the face of methane with a subindex containing the symmetry group (G) of the complex (see the top model in Fig. 2). Another four CH bonded complexes (HX_G) lead to two C_{3v} complexes ($\mathrm{HN}_{C_{3v}}$ and $\mathrm{HO}_{C_{3v}}$) and two C_s complexes (HN_{C_s} and HO_{C_s}). The C_{3v} complexes can be obtained in orientations a and b with $\alpha=0°$ and $\alpha=180°$ for the Y orientated and X orientated complexes, respectively, and in orientation c with $\beta=0°$ and $\beta=180°$ corresponding to $\mathrm{N}_{C_{3v}}$ and $\mathrm{O}_{C_{3v}}$ complexes, respectively (see Fig. 2).

Firstly, the dependencies of the interaction energies with respect to intermolecular distance in the four C_{3v} complexes ($\mathrm{N}_{C_{3v}}$, $\mathrm{O}_{C_{3v}}$, $\mathrm{HN}_{C_{3v}}$, and $\mathrm{HO}_{C_{3v}}$) were explored (see Fig. 2), assuming the orientations a and b. The $R_{\mathrm{C-X}}$ distances were varied from 3.0 to 4.5 Å each at 0.1 Å. The interaction energies at $R_{\mathrm{C-X}}=5$, 6, 7, and 10 Å were also calculated. The optimal distance for each surface was used to perform the exploration of the α angular behavior in orientations a and b, considering the C_s paths. The α angles were varied from 60° to 280° using intervals of 20°. The electronic states of these C_{3v} complexes are ^2E. These states are broken when the configuration moves to a C_s one and two nondegenerate electronic states appear: $^2A'$ and $^2A''$. Both adiabatic surfaces were explored, fixing the intermolecular distance to that determined in the radial curves and the interatomic parameters to the experimental values, as described previously.

The coordinates employed resemble Jacobi coordinates with the intermolecular N–O distance fixed. The β angular variable connects through the $\mathrm{O}_{C_{3v}}$ configuration both C_s CH_3 face complexes (N_{C_s} and O_{C_s}), which are in turn the most stable. The mass center of NO molecule is located at 0.614 and 0.537 Å of N and O atoms, respectively. In this case a bidimensional PES was calculated for A' and A'' electronic states, and $R_{\mathrm{C-MC}}$ was varied from 3.4 to 4.3 Å each at 0.2 Å and β from 0° to 360° each at 20°. Additionally, other points were calculated to improve the surfaces on well regions and also to evaluate the vibration frequencies. These points correspond to $\beta=70°$, 90°, 270°, and 290° for $R_{\mathrm{C-MC}}=3.6$ Å and $\beta=80°$ and 280° for $R_{\mathrm{C-MC}}=3.2$, 3.3, and 3.5 Å in the A'' surface. In the A' surface the additional calculated points correspond to $\beta=100°$ and 260° for $R_{\mathrm{C-MC}}=3.2$, 3.3, and 3.5 Å.

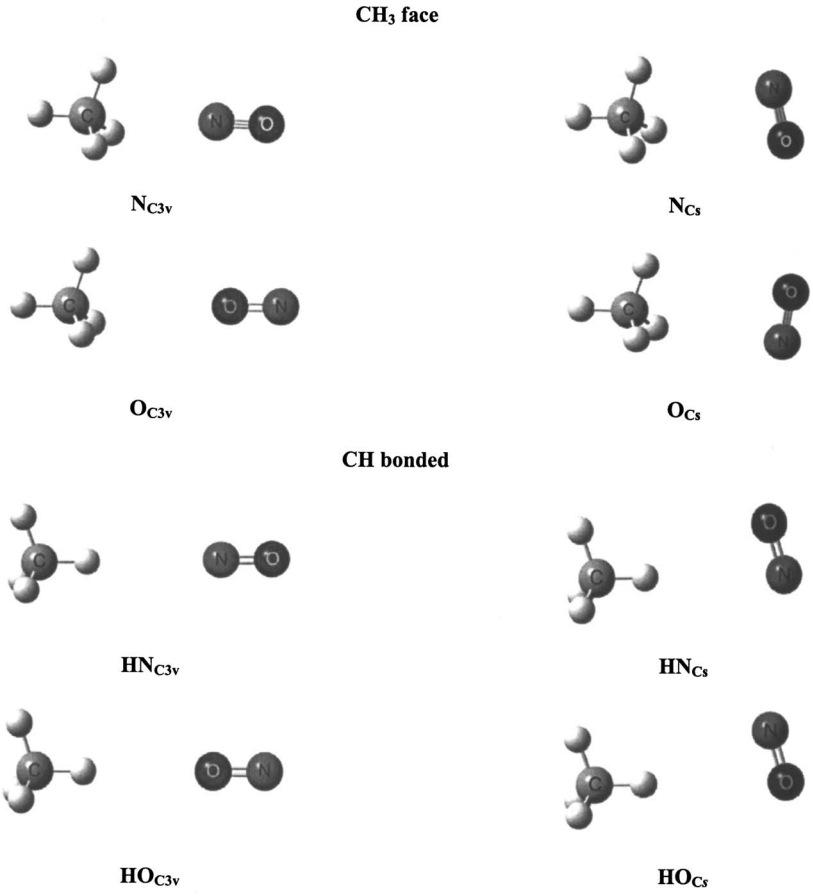


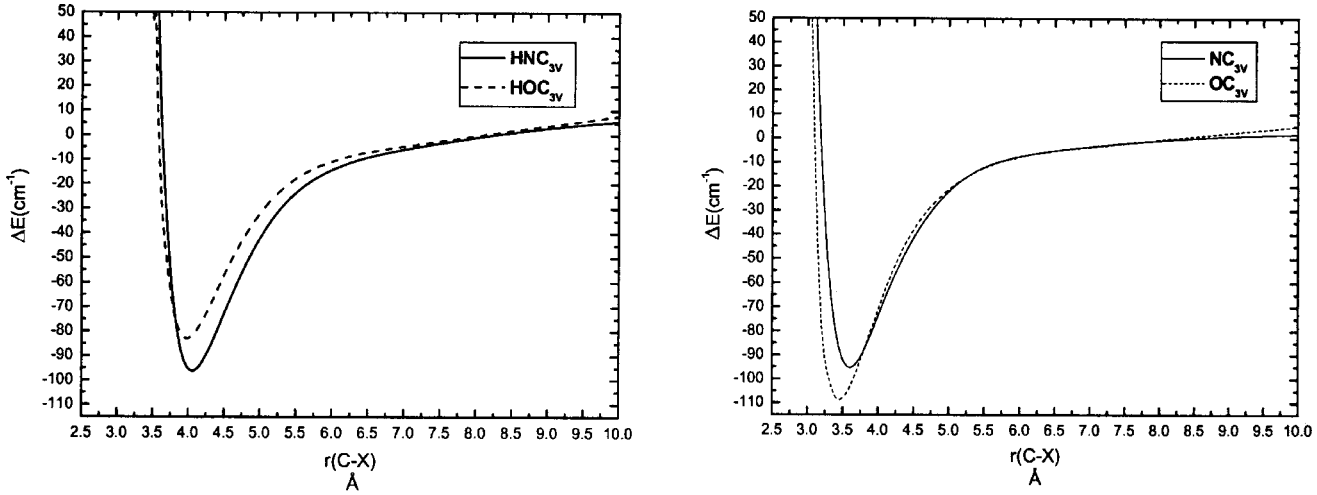
FIG. 2. Nomenclature of CH_3 face and CH bonded complexes with C_{3v} and C_s symmetries.

III. RESULTS AND DISCUSSIONS

The calculation of the C_{3v} complexes was performed employing the A' symmetry for the wave function. The degeneracy of the A' and A'' was checked at selected geometries and artificial symmetry breaking was not found. The radial PES's for the C_{3v} complexes are shown in Fig. 3. These curves were fitted by means of exp-6 curve.[21]

$$E = A\exp(-Br) - \frac{C}{r^6}. \quad (1)$$

The values of A, B, and C parameters and their relative errors are shown in Table I. The intermolecular equilibrium distances to C atom in the CH_3 face complexes are smaller than those in the CH bond complexes. Moreover, the estimated intermolecular distances are smaller in ON orientated com-



a) CH bonded complexes

b) CH_3 face complexes

FIG. 3. Interaction energies (cm^{-1}) vs intermolecular distance R_{C-X} (Å) for the C_{3v} configurations (X=N or O). (a) CH bonded complexes; (b) CH_3 face complexes.

TABLE I. Calculated and fitted parameters for the $E=A\exp(-Br)-C/r^6$ functional form of C_{3v} $CH_4\cdots XY$ (X, Y=N, O) complexes. In parentheses, percentage of relative error; in brackets, the results obtained with the fitted model.

Complexes	A (cm^{-1})	B ($Å^{-1}$)	C ($Å^6$)	r_e(C–X) (Å)	D_e (cm^{-1})
$N_{C_{3v}}$	30 374 352.6(3.14)	3.5408 (0.36)	398 902.2 (0.75)	3.60 [3.62]	98.3 [94.9]
$O_{C_{3v}}$	36 494 796.5(1.67)	3.7250 (0.19)	344 229.3 (0.32)	3.50 [3.45]	108.7 [108.4]
$HN_{C_{3v}}$	85 381 406.9(2.62)	3.4279 (0.31)	771 842.8 (0.90)	4.10 [4.08]	96.2 [95.3]
$HO_{C_{3v}}$	116 044 903.2(2.86)	3.6294 (0.32)	572 232.5 (0.80)	4.00 [3.99]	82.9 [82.1]

plexes than in NO orientated complexes (see Table I). At the RCCSD(T)/aug-cc-pVTZ level, the BSSE correction does not change significantly the shape of the explored adiabatic PES. As expected, their main effect is detected for the intermolecular distances. The intermolecular distances for the $HN_{C_{3v}}$ and $HO_{C_{3v}}$ complexes on the corrected CP MP2/aug-cc-pVTZ PES are in very good agreement with those obtained at the RCCSD(T) level. For the $HN_{C_{3v}}$ complex, N–H distance is of 2.99 Å in the MP2 PES (Ref. 13) and 3.00 Å in the fitted RCCSD(T) CP corrected surface; the values for O–H distances are 2.90 and 2.91 Å, respectively. As expected, the intermolecular distances in the uncorrected CP surfaces are smaller than those obtained in the corrected ones.[11,13]

A. Orientations a and b

According to the calculations when using orientations a and b, there is JT symmetry breaking at least for the most

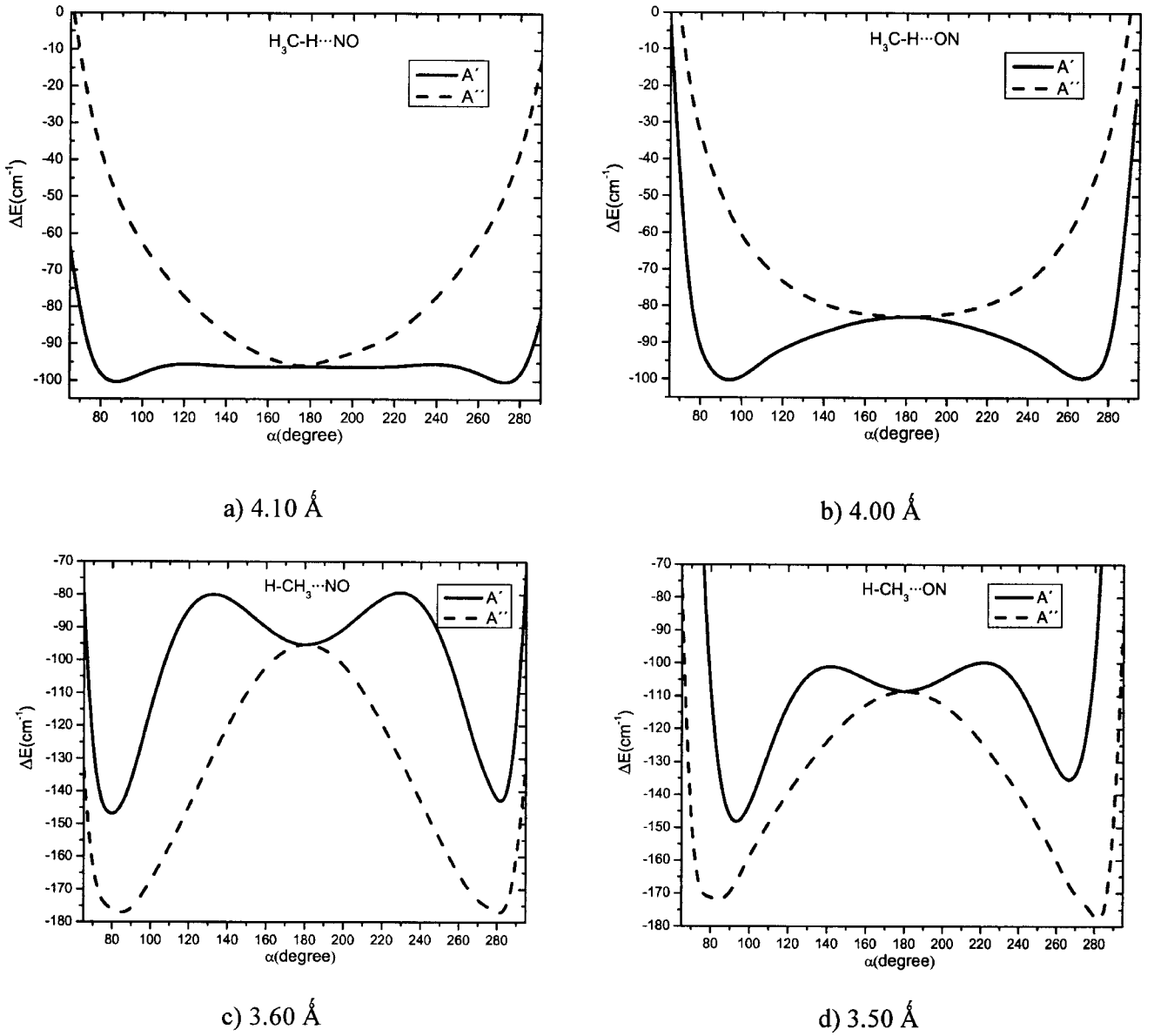


FIG. 4. Interaction energies (cm^{-1}) vs α angle (°) at fixed intermolecular distance R_{C-X} (Å) or C_{3v} stationary points: (a) 4.10, (b) 4.00, (c) 3.60, and (d) 3.50 Å.

TABLE II. Interaction energies (cm^{-1}) for minima of C_s symmetry (orientations a and b).

	HN_{C_s}	HO_{C_s}	N_{C_s}		O_{C_s}	
State	A'	A'	A'	A''	A'	A''
Minimum 1	101.3	100.2	146.3	176.6	151.7	170.9
Minimum 2	101.2	98.5	140.0	176.3	139.6	175.8

stable state for each kind of complexes (Fig. 4). The two CH bonded complexes ($HN_{C_{3v}}$ and $HO_{C_{3v}}$) break the symmetry along the α angle leading to a more stable A' state [see Figs. 4(a) and 4(b)]. However, the JT distortion for CH_3 face complexes ($N_{C_{3v}}$ and $O_{C_{3v}}$) along the same coordinate leads to a more stable A'' state [see Figs. 4(c) and 4(d)]. The potential surfaces along these coordinates show analogous topologies to the well-known Renner-Teller topologies of linear molecules. It is interesting to observe and theoretically explain this effect in a rather weakly bound complex with large amplitude bending motions.[22,23]

Therefore, the α angle was explored from 60° to 280°, two C_s minima of the same orientation are obtained for each NO orientation, and these minima are not exactly equivalent. A minimum corresponds to an arrangement with the Y atom close to one H atom and the second minimum with the Y atom at the same distance from both hydrogen atoms (Fig. 2). Nevertheless, for each kind of complexes (CH bonded and CH_3 face), the energy of each minimum is similar. This indicates that a small out of plane rotation does not have an important contribution to the energy of system. Therefore the PES is almost planar with respect to the explored coordinate.

The energy stabilization due to distortion of the CH bonded complexes is smaller than that obtained for the CH_3 face complexes (Table II). The CH bonded complexes have a minimum in the C_{3v} configurations at considered intermolecular distances in the A' surface. In this case, the JT geometry is a conical intersection between the two components of the degenerate electronic state. For these complexes, the energy barrier between $HN_{C_s}-HN_{C_{3v}}$ is of 5 cm^{-1} and between $HO_{C_s}-HO_{C_{3v}}$ is around 17 cm^{-1}. These energy differences are small and taking into account the ZPE, the energy gain due to JT distortion is small in CH bonded complexes.

In both electronic states of the CH_3 face complexes, the C_s configurations are minima. As a consequence, both electronic states are affected by symmetry distortion (Table II). For these geometries, the energy gap between the A' and A'' states is of around 30 cm^{-1} in both orientations. In the case of N orientated complexes, the barriers from the A' state to the C_{3v} configuration ($N_{C_s}-N_{C_{3v}}$) is of 68 cm^{-1} (considering the most stable minimum), and the value from the A' state is of 37.6 cm^{-1}. For the O orientated complexes the $O_{C_s}-O_{C_{3v}}$ gap is of 78 cm^{-1} for the A'' electronic state and 53 cm^{-1} for the A' state.

B. Orientation c

In this orientation, radial and angular variables were explored. The two-dimensional contour plots appear in Fig. 5. The shape of PES's for the A' and A'' states is similar. A cut

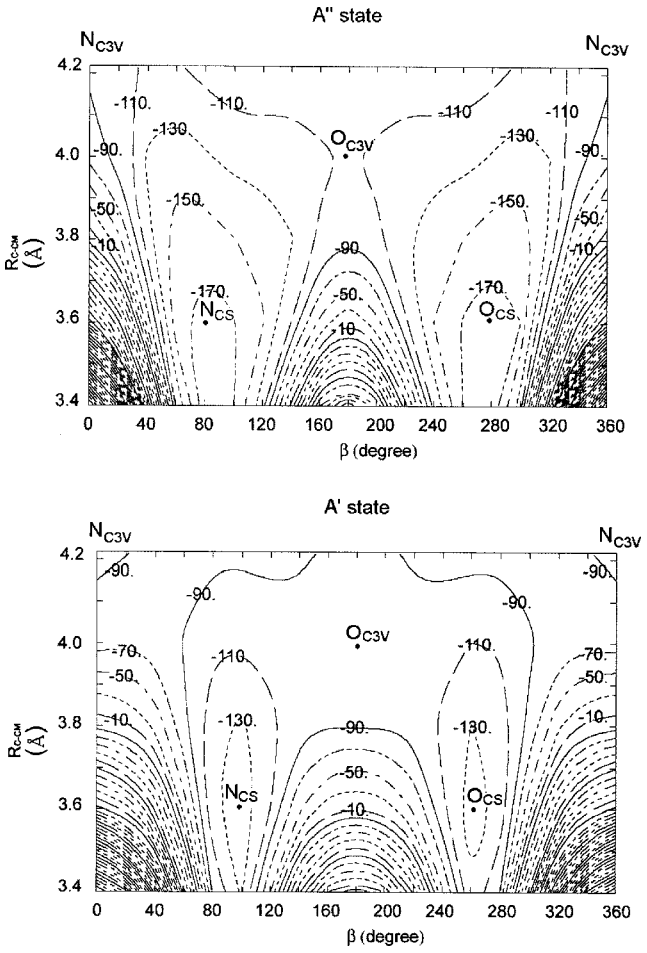


FIG. 5. Two-dimensional contour plots of interaction energies (cm^{-1}) as a function of β angle (°) and R_{C-MC} intermolecular distance (Å).

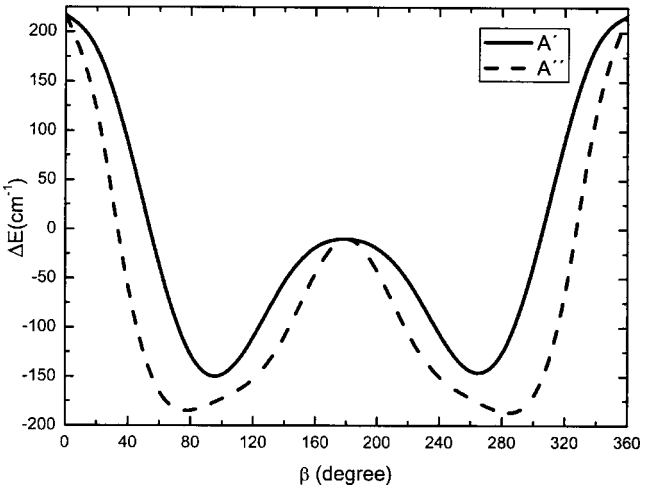


FIG. 6. One-dimensional contour plot of interaction energy (cm^{-1}) vs β angle (°) for the fixed R_{C-MC}=3.60 Å intermolecular distance from Fig. 5.

TABLE III. Interaction energies for C_s stationary points (orientation c).

			Distance to C atom			
	Symmetry	Angle (°)	Mass center (Å)	N (Å)	O (Å)	ΔE (cm^{-1})
N_{C_s}	A'	100	3.6	3.76	3.55	−148.3
O_{C_s}	A'	260	3.6	3.55	3.73	−144.3
N_{C_s}	A''	80	3.6	3.55	3.73	−186.0
O_{C_s}	A''	280	3.6	3.76	3.55	−185.5

of PES for the distance of 3.6 Å is shown in Fig. 6. These graphics clearly show the JT distorsion from the C_{3v} symmetries at both electronic states. The energy stabilization due to JT distortion is larger in the A'' than in the A' surface.

The intermolecular distances obtained are slightly larger than those obtained in Ref. 11 at uncorrected CP MP2/aug-cc-pVTZ PES. For example, the NH distance for the N_{C_s} configuration in the A' state is of around 0.3 Å larger than in the previous study. This enlargement can be mainly due to the effect of BSSE on geometries.

The β coordinate connects the N_{C_s} and O_{C_s} minima through a barrier with C_{3v} symmetry. The energy differences between both minima are of 0.5 and 4 cm^{-1} for the A' and A'' states, respectively. These gaps fall into the error margin of the employed models (see Table III). Hence, both minima can be assumed to be equally stable. This fact reflects that, for these complexes, the CH_4 molecule behaves as a sphere and the model of a three-body system can be assumed for the CH_3 face complexes. In order to calculate the magnitude of ZPE, two body models were considered. The CH_4 was taken as a body with its total mass concentrated in the C atom. For the radial coordinates, a harmonic oscillator model was used. The energy dependence with R_{MC} was adjusted to a parabolic function and the energy levels were obtained. According to these models the frequencies of stretching mode between CH_4 and NO are 60 and 53 cm^{-1} for the A'' and A' states, respectively. For the angular variable, the points of the PES were also fitted to a parabolic function, and the energy levels were calculated assuming the Jacobi coordinate system. The obtained frequencies for the bending mode in the A'' and A' states are 31 and 42 cm^{-1}, respectively. According to these models the ZPEs calculated for the A'' and A' are 46 and 48 cm^{-1}, respectively.

There is a gap of 88 cm^{-1} between the N_{C_s} A'' and $N_{C_{3v}}$ and another gap of 77 cm^{-1} in the $O_{C_{3v}}$ configuration; these energy differences decrease to 50 and 40 cm^{-1} in the A' state. Moreover, the energy gap between both states of N_{C_s} is of 38 cm^{-1}. The ZPE previously estimated for the A'' (46 cm^{-1}) is enough to allow the transition between the A'' and A' states. Also, the ZPE of the A' is in the order of the energy barrier to $O_{C_{3v}}$ configuration. From the above considerations, the $CH_4\cdots NO$ system can be considered to be affected by dynamic JT effect supporting the hypothesis suggested by Musgrave *et al.*[12]

According to the approximations and models used in this work, the computed interaction energies considering the ZPE correction (D_0) are 140 and 100 cm^{-1} for the A'' and A' states, respectively. These results are in good agreement with the experimental D_0 (Ref. 15) for the $\tilde{X}$ state, 103 cm^{-1}.

IV. CONCLUSIONS

According to the employed models, the $CH_4\cdots NO$ complexes in the C_{3v} nuclear arrangements are affected by symmetry distortion. The energy stabilization due to symmetry distortion is smaller in CH bonded complexes than in CH_3 face complexes. An analysis in a two-dimensional PES for the CH_3 face complexes shows that the ZPE is in the order of magnitude of barriers between the C_s and C_{3v} configurations. Therefore, the system is affected by a dynamic JT effect. These results are in agreement with the assumption used for the interpretation of REMPI spectra that considers the $\tilde{X}$ state as an effective C_{3v} symmetry. It is expected that the flatness of the surface allows the transition from N_{C_s} to O_{C_s} through the C_{3v} configurations and particularly through the $O_{C_{3v}}$ complex. The stabilities of both configurations are similar, showing the isotropy of CH_3 face in the considered symmetry plane and also in the nonsymmetrical paths that connect both C_s configurations. The calculated D_0 value is in good agreement with the experimental data.[12,15]

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[1] M. C. Heaven, Annu. Rev. Phys. Chem. **43**, 283 (1992).
[2] Y. Kim and H. Meyer, Int. Rev. Phys. Chem. **20**, 219 (2001).
[3] D. E. Bergeron, A. Musgrave, V. L. Ayles, R. T. Gammon, J. A. E. Silber, and T. G. Wright, J. Chem. Phys. **125**, 144319 (2006).
[4] D. E. Bergeron, A. Musgrave, R. T. Gammon, V. L. Ayles, J. A. E. Silber, T. G. Wright, B. Wen, and H. Meyer, J. Chem. Phys. **124**, 214302 (2006).
[5] J. C. Miller, J. Chem. Phys. **86**, 3166 (1987).
[6] M. Akiike, K. Tsuji, K. Shibuya, and K. Obi, Chem. Phys. Lett. **243**, 89 (1995).
[7] J. Lozeille, S. E. Daire, S. D. Gamblin, T. G. Wright, and E. P. F. Lee, J. Chem. Phys. **113**, 10952 (2000).
[8] S. E. Daire, J. Lozeille, S. D. Gamblin, and T. G. Wright, J. Phys. Chem. A **104**, 9180 (2000).

[9] G. Myszkiewicz and J. Sadlej, Chem. Phys. Lett. **318**, 232 (2000).
[10] S. E. Daire, J. Lozeille, S. D. Gamblin, E. P. F. Lee, and T. G. Wright, Chem. Phys. Lett. **346**, 305 (2001).
[11] S. E. Daire, J. Lozeille, S. D. Gamblin, T. G. Wright, and E. P. F. Lee, Phys. Chem. Chem. Phys. **3**, 917 (2001).
[12] A. Musgrave, D. E. Bergeron, R. J. Wheatley, and T. G. Wright, J. Chem. Phys. **123**, 204305 (2005).
[13] R. Crespo-Otero, L. A. Montero, W. D. Stohrer, and J. M. García de la Vega, J. Chem. Phys. **123**, 134107 (2005).
[14] N. Dozova, L. Krim, M. E. Alikhani, and N. Lacome, J. Phys. Chem. A **110**, 11617 (2006).
[15] D. S. Wright, H. L. Holmes-Ross, and W. D. Lawrance, Chem. Phys. Lett. **435**, 19 (2007).
[16] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
[17] P. J. Knowles, C. Hampel, and H. J. Werner, J. Chem. Phys. **99**, 5219 (1993).
[18] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[19] G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
[20] H.-J. Werner and P. J. Knowles, MOLPRO, version 2006.1, a package of *ab initio* programs, Cardiff, United Kingdom, 2006.
[21] M. Rigby, E. B. Smith, W. A. Wakeham, and G. C. Maitland, *The Forces Between Molecules* (Oxford Science, Oxford, 1986).
[22] M. J. Paterson, M. J. Bearpark, M. A. Robb, L. Blancafort, and G. A. Worth, Phys. Chem. Chem. Phys. **7**, 2100 (2005).
[23] J. J. Dillon and D. R. Yarkony, J. Chem. Phys. **126**, 124113 (2007).