A Theoretical Study of the Cluster Vibrations in Cr_2O_2, Cr_2O_3, and Cr_2O_4

Kai-hua Xiang and Ravindra Pandey*

Department of Physics, Michigan Technological University, Houghton, Michigan 49931

J. M. Recio and E. Francisco

Departamento de Química Física y Analítica, Universidad de Oviedo, 33006-Oviedo, Spain

John M. Newsam

Molecular Simulations Incorporated, San Diego, California 92121

Received: January 12, 1999; In Final Form: December 4, 1999

We report the results of first principles calculations on the Cr_2O_2, Cr_2O_3, and Cr_2O_4 clusters for which some of the considered configurations were proposed in the recent infrared spectroscopy experiments (Chertihin, G. V.; Bare, W. D.; Andrews, L. *J. Chem. Phys.* **1997**, *107*, 2798). Both linear and ring-like isomers are predicted to be equally probable for Cr_2O_2, while the $(Cr_2O_2)O$ isomer is preferred over the chainlike (OCrOCrO) isomer for Cr_2O_3. For Cr_2O_4, a clear preference for the $O(Cr_2O_2)O$ isomer over the $(CrO_2)_2$ isomer is predicted. Calculations of the vibrational frequencies for the lowest energy isomers of these clusters yield the stretching mode involving the stronger Cr−O bond to be around 900−1000 cm^{-1} and the bending mode involving the puckered-ring to be around 550−700 cm^{-1}. Overall, the calculated normal modes of the cluster vibrations provide a very satisfactory description of the observed IR spectrum of the chromia clusters.

1. Introduction

Recently, Chertihin et al.[1] has posed a number of interesting questions concerning the assignment of the vibrational frequencies of the Cr_mO_n ($m = 1-2$, $n = 1-4$) clusters. Some of these questions are related to (i) possibility of coexistence of linear and ring-like isomers for Cr_2O_2, (ii) structural configuration of the lowest-energy isomer of Cr_2O_2 which may involve either a puckered-ring or a Cr−O chain, and (iii) assignment of the observed frequencies to the cluster vibrations of either the $O(Cr_2O_2)O$ isomer or the $(CrO_2)_2$ isomer in Cr_2O_4. In our previous theoretical study of the chromia clusters,[2] the focus was on the role of the oxygen-to-metal ratio in determining structural and electronic properties of these clusters. In this paper, we now focus on the vibrations of the chromia clusters with an aim to provide answers to some of the questions raised by the IR experiments.[1] First, we will begin with total energy calculations of various possible isomers of a given cluster to predict its lowest-energy isomer. The optimized configuration of the lowest energy isomer will then be used to perform the normal-mode analysis of the cluster vibrations of Cr_2O_2, Cr_2O_3 and Cr_2O_4.

2. Computational Model

The computational model used here was described in detail in our earlier study.[2] Briefly, double numeric basis sets were used for chromium and oxygen which were supplemented by diffusion and polarization functions (i.e., 4p for Cr and 3d for O). We also employed the frozen-core approximation, thereby freezing the helium core ($1s^2$) for oxygen and the neon core ($1s^22s^22p^6$) for chromium. Note that these basis sets have been used successfully to study structure and energetics of Cr_2,[3] MgO,[4] and MnO clusters.[5] The nonlocal spin exchange and correlational functionals[6,7] were used in calculations based on density functional theory. The density and energy tolerances were set to 10^{-4} e/bohr^3 and 10^{-6} hartree, respectively. The cluster vibrational frequencies were computed in the harmonic approximation using the fine integration grid[8] and a double-point finite differencing formula with a step size of 0.1 bohr.

For each chromia cluster considered here, the optimized configuration was obtained by searching the symmetry-constrained multidimensional potential energy surface. The calculation was considered to be converged when gradient was less than 10^{-3} hartree/bohr, and variation in total energy was less than 10^{-5} hartree. Frequency calculations were then performed to ascertain the convergence to a local minimum. Among various isomers of a given cluster, an isomer with the lowest total energy was then selected as the ground state of the cluster. It is to be noted here that calculations were not performed for each spin state of the given cluster but the Aufbau principle as implemented in the DMol program[9] was used to obtain the optimal spin state of the cluster.

3. Results and Discussion

3.1. Cluster Configurations. We have considered various configurations of Cr_2O_2 for calculations performing the symmetry-constrained geometry optimization. On the basis of total energy, the planar Cr_2O_2 isomer is predicted to be most stable and is closely followed by the linear CrOCrO isomer. On the other hand, the linear CrOOCr and OCrCrO isomers are found to be higher in energy relative to CrOCrO. Frequency calculations find no imaginary frequencies associated with the planer and CrOCrO isomers whereas the CrOOCr and OCrCrO isomers have few imaginary frequencies in their spectrum. It is interesting to note here that total energy calculations which were started

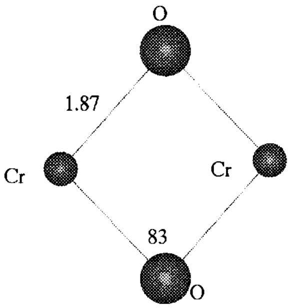
---

* Corresponding author: pandey@mtu.edu.

10.1021/jp990171u CCC: \$19.00

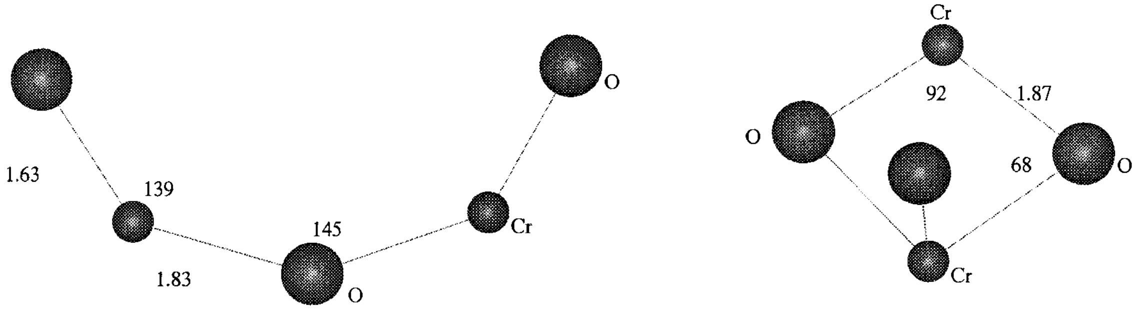
(a) Linear, TE=−2241.88791

(b) Linear, TE=−2242.05901



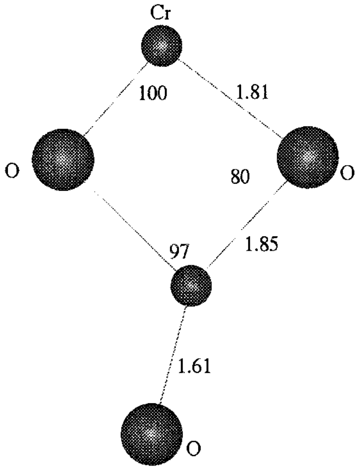
(c) D2h, TE=−2242.05920

Figure 1. Optimized configurations of Cr_2O_2. The unit of total energy (TE) is hartree, and that of the bond length is in angstroms.



(a) C2v, TE=−2317.62339

(b) D3h, TE=−2317.57057



(c) Cs, TE=−2317.63036

Figure 2. Optimized configurations of Cr_2O_3. The unit of total energy (TE) is hartree, and that of the bond length is in angstroms.

with either a nonlinear configuration of O−Cr−O−Cr or a nonplanar configuration have approximately converged to a planar configuration for Cr_2O_2.

As shown in Figure 1, R_{Cr-O} is 1.87 Å in the planar (ring-like) isomer (i.e., Cr_2O_2)), while the linear CrOCrO isomer has two distinct values of 1.81(1.82) Å and 1.66 Å for R_{Cr-O}. The shorter Cr−O bond length is associated with the end oxygen atom and is about the same as in CrO.[2] Table 1 lists total energies of these isomers showing that CrOCrO and (Cr_2O_2) are predicted to be nearly degenerate with an energy difference of 0.005 eV. On the other hand, the OCrCrO isomer is found to be higher in energy by more than 4 eV than the lowest energy isomers indicating the preference of the Cr−O bond over the Cr−Cr bond in the linear configuration. Calculations have

TABLE 1: Total Energy of the Cr_2O_2, Cr_2O_3, and Cr_2O_4 Cluster Configurations

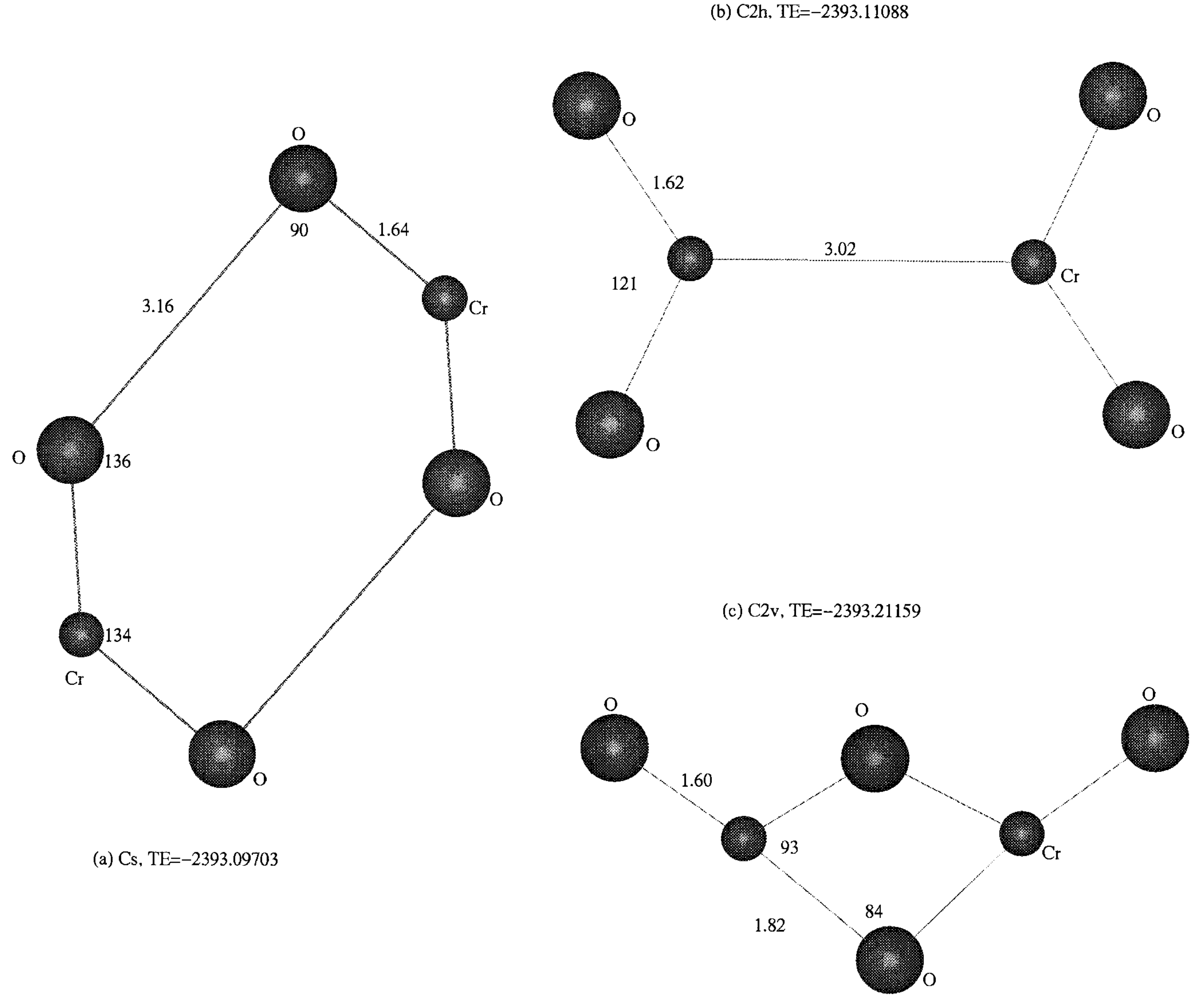
cluster	symmetry	multiplicity ($2S+1$)	total energy (hartree)	relative energy (eV)
Cr_2O_2	D_{2h}-planar	9	−2242.05920	0.0
	$C_{\infty v}$-linear(OCrOCr)	9	−2242.05901	0.005
	$D_{\infty h}$-linear(OCrCrO)[a]	3	−2241.88631	4.7
Cr_2O_3	C_s-non planar	5	−2317.63036	0.00
	C_{2v}-planar	7	−2317.62339	0.19
	$D_{\infty h}$-linear	7	−2317.61488	0.42
	D_{3h}-non planar	5	−2317.57057	1.63
Cr_2O_4	C_{2v}-non planar	3	−2393.21159	0.00
	D_{2h}-planar[a]	5	−2393.11088	2.74
	C_{2h}-planar[a]	1	−2393.09703	3.12

[a] Optimized configuration is not at the local minimum due to the presence of imaginary frequencies.

therefore validated the results of the IR experiments[1] indicating the formation of both CrOCrO and (Cr_2O_2) isomers during the reaction of the laser-ablated Cr with O_2 in solid argon.

Isomers of the Cr_2O_3 cluster can be generated by adding an oxygen atom to the planar (Cr_2O_2) isomer. The resulting nonplanar (Cr_2O_2)O configuration can have either D_{3h} or C_s symmetry as shown in Figure 2. Calculations predict that the highly symmetric D_{3h} isomer is not energetically preferred over the isomer with the C_s symmetry. In an alternative way, we can also add oxygen to the linear CrOCrO isomer yielding the planar (chainlike) OCrOCrO configuration with the C_{2v} symmetry. As shown in Table 1, the energy difference between OCrOCrO and (Cr_2O_2)O is predicted to be small (0.2 eV). The calculated results therefore corroborate the IR experimental results in predicting the formation of either a puckered ring with a terminal oxygen atom (i.e., (Cr_2O_2)O)) or a chainlike (i.e., OCrOCrO) isomer for Cr_2O_3. We note here that both isomers show the presence of the strong Cr−O bond which is manifested by the two distinct Cr−O bond lengths of 1.63 and 1.83 Å in OCrOCrO and 1.61 Å and 1.81(1.85) Å in (Cr_2O_2)O (Figure 2).

For Cr_2O_4, a cluster configuration can be generated by adding one oxygen atom to the (Cr_2O_2)O isomer either in a cis- or in a trans-position. The optimized configuration, independent of the choice of the initial (cis- or trans-) geometry, shows that the two terminal oxygens in O(Cr_2O_2)O prefer to be cis to one another rather than trans (Figure 3). The calculated results therefore show that the trans geometry is not a local minimum for the O(Cr_2O_2)O isomer. The other possible isomers for Cr_2O_4 can be constructed from two CrO_2 fragments joined either via the Cr−Cr bond forming the ethylene-like configuration of the D_{2h} symmetry or via the O−O bond forming the six-membered



(b) C2h, TE=−2393.11088

(c) C2v, TE=−2393.21159

(a) Cs, TE=−2393.09703

Figure 3. Optimized configurations of Cr_2O_4. The unit of total energy (TE) is hartree, and that of the bond length is in angstroms.

TABLE 2: Comparison of the Calculated IR Active Modes for Clusters in Vacuo and the Observed Frequencies for Clusters Trapped in Solid Argon

this work			experiment (ref 2)	
calculated frequency (cm^{-1})	assignment[a]	isomer	observed frequency (cm^{-1})	assignment
1015	stretching	$O(Cr_2O_2)O$		
975	stretching	$O(Cr_2O_2)O$		
971	stretching	$(Cr_2O_2)O$	1044.8	Cr_2O_3
925	stretching	OCrOCrO		
921	stretching	OCrOCrO		
889	stretching	CrOCrO	984.3	CrOCrO
831.3w	$(Cr_2O_2)O$			
724	bending	OCrOCrO		
701	bending	$O(Cr_2O_2)O$	716.2	$O(Cr_2O_2)O$
694	bending	$(Cr_2O_2)O$	700.8	$(Cr_2O_2)O$
555	bending	$O(Cr_2O_2)O$	643.1	$O(Cr_2O_2)O$
582	bending	Cr_2O_2	628.2	(Cr_2O_2)
374	bending	$(Cr_2O_2)O$		
298	bending	(Cr_2O_2)		

[a] The stretching mode is associated with the stronger Cr−O bond and the bending mode is associated with the ring (Cr_2O_2) in the chromia clusters.

ring configuration with the C_{2h} symmetry. Table 1 lists total energies of these isomers where the preference for $O(Cr_2O_2)O$ is clearly predicted over the isomers based on the CrO_2 fragments. Furthermore, frequency calculations yield imaginary modes of vibrations for the $(CrO_2)_2$ isomers indicating that their optimized configurations do not represent a local minimum. Although $O(Cr_2O_2)O$ has an imaginary mode, its magnitude (15 cm^{-1}) is small enough to suggest that the optimized configuration does indeed represent the ground state of $O(Cr_2O_2)O$.[10]

The puckered-ring (Cr_2O_2) configuration turns out to be a building block of the lowest energy isomers of the Cr_2O_3 and Cr_2O_4 clusters. As we go from Cr_2O_2 to Cr_2O_4, the Cr−O and Cr−Cr bond lengths remain the same in the ring while the O−O bond length decreases from 2.81 to 2.64 Å. On the other hand, the terminal oxygen atoms forms a stronger Cr−O bond with the bond-length of 1.61 Å in Cr_2O_3 and Cr_2O_4. We may therefore conclude that the energetically favorable isomers for larger chromia clusters would prefer the dominance of the Cr−O and O−O bonds over that of the Cr−Cr bond.

This conclusion can be further reinforced by the predicted spin multiplicities for the lowest energy isomers of these clusters. Addition of oxygen to Cr_2O_2 facilitates the pairing of electrons in the Cr-3d orbital with those in the O-2p orbital. Consequently, lowering of the spin multiplicity is expected to occur in going from Cr_2O_2 to Cr_2O_4. As shown in Table 1, the spin multiplicities of Cr_2O_2, Cr_2O_3, and Cr_2O_4 are predicted to be nonet,[11] quintet, and triplet for the lowest energy isomers, respectively.

3.2. Cluster Vibrations. We now perform the analysis of the normal modes of the vibrational frequencies of these clusters considering only their lowest energy isomers. These isomers are (Cr_2O_2) and CrOCrO for Cr_2O_2, OCrOCrO and $(Cr_2O_2)O$ for Cr_2O_3, and $O(Cr_2O_2)O$ for Cr_2O_4. In Table 2, we compare the dominant IR active modes with the observed frequencies. A complete list of the calculated normal modes of the cluster vibrations along with their frequencies and intensities is given in Tables 3 and 4.

TABLE 3: The calculated normal modes of the lowest energy isomers of Cr_2O_2 and Cr_2O_3

cluster	isomer	symmetry	mode	frequency (cm^{-1})	intensity
Cr_2O_2	(Cr_2O_2)	D_{2h}	B_{1u}	104	0.2
			B_{3u}	298	0.82
			B_{3g}	316	0.0
			A_g	373	0.0
			B_{2u}	582	1.0
			A_g	641	0.0
	CrOCrO	$C_{\infty v}$	Π	133	0.2
			Π	138	0.2
			Σ^+	313	0.0
			Σ^+	709	0.2
			Σ^+	889	1.0
Cr_2O_3	OCrOCrO	C_{2v}	A_2	71	0.0
			B_2	87	0.2
			A_1	91	0.0
			B_1	150	0.1
			A_1	251	0.1
			A_1	381	0.0
			B_1	724	1.0
			B_1	921	0.6
			A_1	925	0.9
	$(Cr_2O_2)O$	C_s	A'	124	0.2
			A''	215	0.1
			A'	269	0.1
			A'	308	0.0
			A'	374	0.84
			A''	459	0.1
			A'	690	0.0
			A''	694	0.4
			A'	971	1.0

TABLE 4. Calculated Normal Modes of the Lowest-Energy Isomer of Cr_2O_4

cluster	isomer	symmetry	mode[a]	frequency (cm^{-1})	intensity
Cr_2O_4	$O(Cr_2O_2)O$	C_{2v}	B_2	141	0.0
			A_2	209	0.0
			B_1	219	0.0
			A_1	345	0.0
			A_1	358	0.0
			A_2	410	0.0
			B_2	555	0.3
			A_1	686	0.0
			B_1	701	0.4
			B_2	980	1.0
			A_1	1015	0.3

[a] Calculations find an imaginary mode of magnitude of 15 cm^{-1} associated with this isomer.

The dominant IR active modes of the Cr_2O_2 isomer are associated with the asymmetric bending mode of the ring at 582 and 298 cm^{-1}. On the other hand, the linear CrOCrO isomer has an active mode at 889 cm^{-1} associated with the symmetrical stretching mode of the stronger Cr−O bond ($R_{Cr-O} = 1.61$ Å). Experimentally, the cluster vibration at 628.2 s suggested to be associated with the ring-like, whereas the band at 984.3 cm^{-1} is definitively assigned to the linear isomer of Cr_2O_2 based on isotopic splittings. The calculated results are therefore consistent with the experimental assignments considering that calculations predict coexistence of both isomers for Cr_2O_2.

In Cr_2O_3 the planar OCrOCrO isomer has the active modes at 925, 921, and 724 cm^{-1} while the nonplanar $O(Cr_2O_2)$ isomer has the active modes at 971, 694, and 374 cm^{-1}. The higher frequency modes (>900 cm^{-1}) in both isomers are identified due to stretching of the stronger Cr−O bond (Figure 2). The remaining modes are predicted to be associated with the bending modes of the isomers. Although the observed peaks at 1044.8 and 700.8 cm^{-1} are suggested to be due to the cluster vibrations of Cr_2O_3, Chertihin et al.[1] have made only their assignments tentatively. Comparison with calculations suggests the association of the first peak with a stretching mode of the OCrOCrO isomer, while that of the second peak with a bending mode of the puckered-ring of the $(Cr_2O_2)O$ isomer. Calculations, however, do not provide the assignment for the weak band observed at 831.3 cm^{-1}. Chertihin et al.[1] suggested it to be associated with the terminal Cr−O vibrations of the $(Cr_2O_2)O$ configuration. In contrast to this suggestion, calculations find such a stretching mode to be around 900−1000 cm^{-1}.

In Cr_2O_4, the lowest energy configuration corresponds to $O(Cr_2O_2)O$ where two terminal oxygens are end-bonded to Cr_2O_2. Here, the calculated IR active modes in the high-frequency regime are associated with the stretching mode of terminal oxygens. The calculated mode at 1015 cm^{-1} is associated with the symmetrical stretching whereas the mode at 980 cm^{-1} is due to the asymmetrical stretching. The other IR active modes in $O(Cr_2O_2)O$ are at 701 and 555 cm^{-1} and are found to be associated with the bending of the puckered-ring. Experimentally, the bending modes are observed at 716.2 and 643.1 cm^{-1}. Although none of the observed IR bands are assigned to the stretching modes of the $O(Cr_2O_2)O$ isomer, the bending mode frequencies clearly indicate the existence of a cluster having two equivalent Cr atoms and two sets of equivalent pairs of O atoms,

The well-characterized bands in the IR experiment[1] on Cr_2O_2, Cr_2O_3, and Cr_2O_4 clusters appear to be at 984.3(CrOCrO), 716.2 ($O(Cr_2O_2)O$), and 643.1 cm^{-1} ($O(Cr_2O_2)O$). The corresponding calculated values are 889, 701 and 555 cm^{-1} indicating deviations of about 10%, 2%, and 14% respectively. Considering that the IR frequencies were obtained on clusters trapped in solid argon and calculations were performed for clusters in vacuo, the agreement between theory and experiment seems to be good. The difference between vibrational frequencies obtained from matix isolated cluster and gas phase cluster is generally expected. For example, a symmetric stretching frequency of matrix isolated CrO_2 is reported to be in the range of 914-960 cm^{-1} while that of gas-phase CrO_2 is measured to be at 895 ± 20 cm^{-1}.[12]

Chertihin et al.[1] have also observed few IR absorption bands which were not assigned to specific chromia clusters. The observed (unassigned) bands at 1027.2, 956.8, 934.3 cm^{-1} are expected to be associated with the Cr−O stretching mode since the present calculations predict the stretching mode to be more than 900 cm^{-1}. In the OCrOCrO isomer of Cr_2O_3, calculations yield two dominant stretching modes at about 925 and 921 cm^{-1} which may be related to two closely spaced frequencies observed at 956.8 and 934.3 cm^{-1} respectively. On the other hand, the observed band at 1027.2 cm^{-1} may tentatively be assigned to the Cr−O stretching mode of the $O(Cr_2O_2)O$ isomer of Cr_2O_4 which was calculated to be at 1015 cm^{-1}. We note here that the calculated frequencies in the low-frequency region (<500 cm^{-1}) are not generally observed in experiments.

3.3. Summary. The calculated results confirm the feasibility of a coexistence of the linear and ring-like isomers for Cr_2O_2 and predict the preference of a puckered-ring configuration with terminal oxygens over the ethylene-like configuration for Cr_2O_4. Assignments have also been mode for the cluster vibrations in Cr_2O_3. Overall, analysis of the computed vibrational frequencies finds the stretching mode of the Cr−O bond to be around 900−1000 cm^{-1}, and the bending mode of the puckered-ring to be around 550−700 cm^{-1}. Furthermore, the expected correlation between R_{Cr-O} and the frequency of the stretching mode is revealed; the shorter the R_{Cr-O} distance the higher the frequency.

Acknowledgment. The authors acknowledge the support from NATO collaborative Grant CRG921348 and Spanish DGICYT, Project PB96-0559.

References and Notes

(1) Chertihin, G. V.; Bare, W. D.; Andrews, L. *J. Chem. Phys.* **1997**, *107*, 2798.

(2) Veliah, S.; Xiang, K.; Pandey, R.; Recio, J. M.; Newsam, J. *J. Phys. Chem. B* **1998**, *102*, 1126.

(3) Delley, B.; Freeman, A. J.; Ellis, D. E. *Phys. Rev. Lett.* **1983**, *50*, 488.

(4) Veliah, S.; Pandey, R.; Li, Y.; Newsam, J.; Vessal, B. *Chem. Phys. Lett.* **1995**, *235*, 53.

(5) Nayak S. K.; Jena P. **1999**. Unpublished.

(6) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* (*Canada*) **1980**, *58*, 1200.

(7) Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098.

(8) In the earlier work,[2] we used the medium grid for frequency calculations. For CrO, the use of the medium grid yields the frequncy to be 884 cm^{-1} while the use of the fine grid results in the value of 879 cm^{-1}.

(9) *DMol user guide*, version 2.3.6; Molecular Simulations, Inc.: San Diego, CA, 1995.

(10) We believe that numerical uncertainities in the computation of the second derivative may be a source of this small value of the calculated imaginary mode.

(11) Note that our earlier work[2] considered the spin states up to septet for Cr_2O_2.

(12) Wenthold, P. G.; Jonas, K.-L.; Lineberger, W. C. *J. Chem. Phys.* **1997**, *106*, 9961.