

Comment on “Infrared spectrum and theoretical study of the dinitrogen pentoxide molecule (N₂O₅) in solid argon” [J. Chem. Phys. 104, 7836 (1996)]

Ilya Zhun, Xuefeng Zhou, and Ruifeng Liu

Citation: *The Journal of Chemical Physics* **105**, 11366 (1996); doi: 10.1063/1.472986

View online: <http://dx.doi.org/10.1063/1.472986>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/105/24?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Ab initio study of NO₂. V. Nonadiabatic vibronic states and levels of the X ²A₁ / ²B₂ conical intersection](#)
J. Chem. Phys. **105**, 9051 (1996); 10.1063/1.472762

[Geometric structure of Ar·NO⁺: Revisited. A failure of density functional theory](#)
J. Chem. Phys. **105**, 7579 (1996); 10.1063/1.472597

[Fourier transform infrared and theoretical isotopic study of the ν₄\(σ_u\) and ν₅\(σ_u\) modes of linear C₇](#)
J. Chem. Phys. **105**, 5313 (1996); 10.1063/1.472400

[Infrared spectrum and theoretical study of the dinitrogen pentoxide molecule \(N₂O₅\) in solid argon](#)
J. Chem. Phys. **104**, 7836 (1996); 10.1063/1.471500

[Ab initio prediction of gas phase molecular structure of 1-chlorosilatrane](#)
AIP Conf. Proc. **330**, 241 (1995); 10.1063/1.47696



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Comment on "Infrared spectrum and theoretical study of the dinitrogen pentoxide molecule (N_2O_5) in solid argon" [J. Chem. Phys. 104, 7836 (1996)]

Ilya Zhun, Xuefeng Zhou, and Ruifeng Liu

Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 37614-0695

(Received 23 July 1996; accepted 17 September 1996)

[S0021-9606(96)00248-6]

In a recent article,¹ the matrix IR spectra of dinitrogen pentoxide (N_2O_5) were reported and compared to earlier solid and gas phase spectra as well as results of density functional theory (DFT) and *ab initio* MP2 calculations. The spectral features compare favorably with other experimental results,² but were found in disagreement with theoretical predictions. It was concluded that more sophisticated calculations that are impossible today are most valuable for understanding the problem. As DFT has been found to give satisfactory prediction of the structural and spectral features of many nitrogen oxides,³ and in order to understand the performance of DFT as a general approach to molecular properties, we decided to carry out a detailed DFT study on the structure and vibrational spectrum of N_2O_5 .

All our calculations were carried out using Gaussian94 program package⁴ employing Becke's three-parameter hybrid DFT/HF method with Lee–Yang–Parr correlation functional (B3LYP) and the 6-31G* and 6-311+G(2d) basis sets. The calculated structural parameters are compared with results of electron diffraction study⁵ in Fig. 1. As is shown that the results obtained with the 6-31G* and 6-311+G(2d) basis sets are remarkably close, indicating that the B3LYP/6-31G* structural parameters are essentially converged with respect to basis set expansion. The calculated results are in excellent agreement with experimental structural parameters. The largest difference between the calculated and electron diffraction bond lengths is smaller than 0.01 Å, and the largest difference between the calculated and electron diffraction bond angles is about 2°. The calculated O–N–O–N dihedral angle, 31°, is in good agreement with the electron diffraction result, 30°, thus confirming the experimental value. The largest deviation between the calculated and electron diffraction bond angles is found for the N–O–N angle for which the experimental result is associated with a larger than usual uncertainty.⁵

The calculated vibrational frequencies and IR intensities are compared with the latest matrix IR results of Bencivenni *et al.*¹ in Table I. Note that in this table the observed frequencies were assigned on the basis of the calculated results which are in agreement with the DFT results of Stirling *et al.*³ All the experimental and theoretical studies are in agreement in the assignment of the NO_2 stretching fundamentals (ν_1 , ν_2 , ν_9 , and ν_{10}), but there are some controversies on the assignments of the rest of the fundamentals. For example, all the experimental studies assigned the band at

863 cm^{-1} to asymmetric N–O–N stretching, but all previous and the present DFT calculations indicate it is much closer to the calculated in-phase symmetric NO_2 bending mode. The asymmetric N–O–N stretching mode is predicted by DFT calculations to be around 350 cm^{-1} and is likely the observed band at 344 cm^{-1} . The band at 737 cm^{-1} was assigned to in-phase NO_2 rocking by Hisatsune *et al.*,² to asymmetric NO_2 bending by Stirling *et al.*,³ and to symmetric NO_2 bending by Bencivenni *et al.*¹ Our calculated results indicate it is asymmetric NO_2 bending, thus in agreement with the assignment of Stirling *et al.* The assignment of the observed frequencies given in Table I is supported by good agreement between the calculated and observed $^{15}\text{N}_2$ isotope shifts. Compared to the ten observed isotope shifts of $^{15}\text{N}_2$ substitution, only two of the calculated results differ by more than 2 cm^{-1} from the experimental results. For ν_5 , both calculations and experiments indicate it is a very weak band, which might contribute to the difficulties in experimental measurement. The difference between the calculated and observed $^{15}\text{N}_2$ isotope shifts of ν_{14} is 7 cm^{-1} . The origin of this discrepancy is unclear yet.

Bencivenni *et al.*¹ attempted to measure the frequencies of NO_2 – ^{18}O – NO_2 by reacting NO_2 with $^{18}\text{O}_3$ and taking matrix IR spectrum of the product. Their observed isotope shifts are presented in the last column of Table I. It is shown that the calculated isotope shifts of NO_2 – ^{18}O – NO_2 are not even in qualitative agreement with the observed results. On the other hand, the calculated isotope shifts of

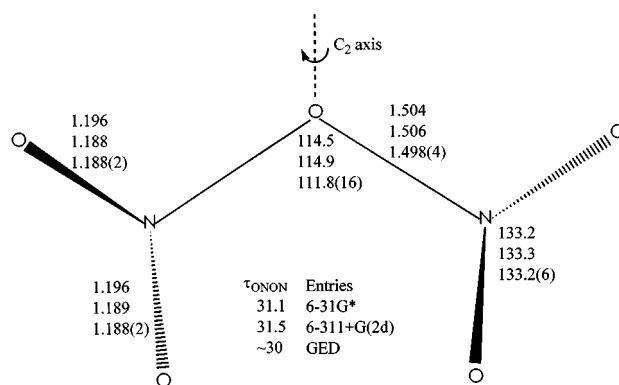


FIG. 1. B3LYP and gas-phase electron diffraction structures of N_2O_5 . (Bond lengths are given in Å and angles in degrees. The experimental data are taken from Ref. 5, values in parentheses are estimated uncertainties.)

TABLE I. Calculated^a and observed vibrational frequencies of N₂O₅.^b

Sym.	ν	DFT1		DFT2		Expt.		Mode description ^c	$\Delta\nu$ - ¹⁵ N ₂ ^d			$\Delta\nu$ - ¹⁸ O ^e		$\Delta\nu$ - ¹⁸ O ^f		$\Delta\nu$ - ¹⁸ O ^g
		Freq.	I_{IR}	Freq.	I_{IR}	Freq.	I_{IR}		DFT1	DFT2	Expt.	DFT1	DFT2	DFT1	DFT2	
a	1	1856	375.4	1792	461.3	1742	1	N=O asym. str.	43	41	40	0	0	5	5	0
	2	1412	43.06	1382	40.76	1339	0.07	N=O sym. str.	17	16	18	0	0	12	12	11
	3	886	29.04	886	25.83	863	0.02	NO ₂ sym. bend.	11	12	10	7	8	4	4	6
	4	804	0.84	811	1.65			wag. + NO ₂ bend.	12	13		10	9	4	4	
	5	675	0.17	683	0.09	640	0.02	NO ₂ rock. + wag.	10	9	15	11	12	2	3	0
	6	385	0.82	381	1.61			N-O-N sym. str.	3	2		2	2	8	7	
	7	227	0.46	219	0.38			N-O-N bend.	0	1		1	1	0	1	
	8	62	0.29	62	0.34			tor.	0	0		0	0	0	1	
b	9	1812	306.7	1792	461.3	1703	0.5	N=O asym. str.	41	41	40	0	0	5	5	0
	10	1313	361.7	1286	353.9	1243	0.35	N=O sym. str.	9	7	8	2	2	16	16	15
	11	750	318.6	753	282.9	737	0.5	NO ₂ sym. bend.	9	9	9	1	2	6	7	7
	12	726	21.91	740	19.19	715	0.02	wag.	17	18	17	4	4	2	2	0
	13	572	276.8	568	288.2	569	0.3	NO ₂ rocking	3	3	2	18	16	2	2	2
	14	360	250.8	345	332.6	344	0.3	N-O-N asym. str.	3	3	10	7	7	1	0	0
	15	47	2.09	48	2.32			tor.	0	0		1	1	0	1	

^aBy B3LYP with 6-31G* (DFT1) and 6-311+G(2d) (DFT2) basis sets. Frequencies are given in cm⁻¹, and IR intensities in km/mole.

^bMatrix FTIR results of Bencivenni *et al.*, Ref. 1. The IR intensities are relative to the strongest band at 1742 cm⁻¹.

^cAccording to total vibrational energy distribution (TED) analysis.

^dIsotope shifts of ¹⁵N substitution in cm⁻¹.

^eIsotope shifts of ¹⁸O substitution of the central oxygen atom (NO₂-¹⁸O-NO₂).

^fIsotope shifts of ¹⁸O substitution of an oxygen atom at NO₂ moiety (NO₂-O-NO¹⁸O).

^gObserved isotope shifts of the product of reaction between NO₂ and ¹⁸O₃ in solid Ar matrix, Ref. 1.

NO₂-O-NO¹⁸O (the four oxygen atoms of the NO₂ moieties in N₂O₅ are nearly equivalent according to the calculations) are in satisfactory agreement with the observed results, indicating the major product of the reaction between NO₂ and ¹⁸O₃ is more likely NO₂-O-NO¹⁸O instead of NO₂-¹⁸O-NO₂. As there are four nearly equivalent oxygen atoms on the NO₂ moieties versus only one bridging oxygen atom, formation of NO₂-O-NO¹⁸O is clearly favored statistically.

In summary, results presented in Fig. 1 and Table I indicate that the B3LYP functional with both the 6-31G* and 6-311+G(2d) basis sets predicts the structural and spectral features of N₂O₅ accurately. The discrepancies between the DFT and observed frequencies of Bencivenni *et al.* are due to their incorrect assignment of the observed IR bands. Agreement between the calculated and observed isotope shifts suggests that the major product of the reaction between NO₂ and ¹⁸O₃ is more likely NO₂-O-NO¹⁸O instead of NO₂-¹⁸O-NO₂.

This study was supported by the Research and Develop-

ment Committee of East Tennessee State University and Research Corporation. IZ is grateful to the Office of Sponsored Research and Programs of East Tennessee State University for financial support.

¹L. Bencivenni, N. Sanna, L. Schriver-Mazzuoli, and A. Schriver, *J. Chem. Phys.* **104**, 7836 (1996).

²I. C. Hisatsune, J. P. Devlin, and Y. Wada, *Spectrochim. Acta* **18**, 1641 (1962).

³A. Stirling, I. Papai, J. Mink, and D. R. Salahub, *J. Chem. Phys.* **100**, 2910 (1994).

⁴Gaussian 94, Revision B.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

⁵B. W. McClelland, L. Hedberg, K. Hedberg, and K. Hagen, *J. Am. Chem. Soc.* **105**, 3789 (1983); B. W. McClelland, Ph.D. Dissertation, Oregon State University, Corvallis, Oregon (1971).