

AN ACCURATE QUARTIC FORCE FIELD AND FUNDAMENTAL FREQUENCIES FOR THE OZONIDE ANION: A RARE POSITIVE ANHARMONICITY FOR THE ANTISYMMETRIC STRETCH

Timothy J. LEE^{a,*}, Christopher E. DATEO^b, Mercedes RUBIO^c and Björn O. ROOS^d

^a MST27B-1, NASA Ames Research Center, Moffett Field, CA 94035-1000, U.S.A.; e-mail: tjlee@mail.arc.nasa.gov

^b Eloret Corporation, MST27B-1, NASA Ames Research Center, Moffett Field, CA 94035-1000, U.S.A.; e-mail: cdateo@mail.arc.nasa.gov

^c Departamento de Química Física, Instituto de Ciencia Molecular, Universitat de València, Dr. Moliner 50, Burjassot, ES-46100 Valencia, Spain; e-mail: mercedes.rubio@uv.es

^d Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden; e-mail: bjorn.roos@teokem.lu.se

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The CCSD(T) method has been used to compute a highly accurate quartic force field and fundamental frequencies for all ¹⁶O and ¹⁸O isotopomers of the ozonide anion. The CCSD and CASPT2 methods have also been used to verify the reliability of the CCSD(T) fundamental frequencies. The computed fundamental frequencies are in agreement with gas-phase experiments, but disagree with matrix isolation experiments for the antisymmetric stretch, ν_3 . CASPT2 calculations show that the antisymmetric part of the O₃⁻ potential surface is sensitive to the external environment. It is concluded that the antisymmetric stretch exhibits a significant matrix shift in the matrix isolation experiments and that the matrix environment is not representative of the gas-phase environment for ozonide anion. It is hoped that the theoretical data provided here will aid in the interpretation of future high-resolution gas-phase experiments.

Keywords: Ozone; Ozonide; Isotope effects; *Ab initio* calculations; Vibrational spectroscopy; CCSD.

The negative ion of ozone, ozonide, has attracted some attention recently because of its unusual photodissociation dynamics^{1,2}. Ozonide is also of interest because of its importance in the Earth's ionosphere, and as such it has been the subject of several experimental and theoretical studies over

the past 30 years (see, refs^{3,4} and references therein). Characterization of the molecular properties of ozonide, including its infrared (IR) spectrum, has been the subject of most of these earlier studies. The vibrational spectrum of the ozonide anion has been studied using both experimental⁵⁻⁷ and theoretical approaches^{2,3}. The experimental studies can be grouped into gas-phase and matrix isolation studies – see ref.³ for a brief review of work on O_3^- prior to 1995. The agreement between the gas-phase and matrix isolation studies for the fundamental vibrational frequencies of ozonide is reasonably good with the exception of the antisymmetric stretch (see the summary data compiled by Jacox⁸). Matrix isolation experiments have consistently obtained a value for the antisymmetric stretch in the range of 789–804 cm^{-1} , while the low-resolution gas-phase experiment obtained a value of $880 \pm 50 \text{ cm}^{-1}$.

The theoretical calculations so far have all been at the harmonic approximation. Of these calculations, the highest levels of theory³ have supported the gas-phase assignment over the matrix isolation value. The CASPT2 method using a large [5s4p3d2f] atomic natural orbital (ANO) basis set obtained a value of 879 cm^{-1} , while a restricted CCSD(T) approach using the cc-pVTZ basis set obtained a value of 911 cm^{-1} . It was speculated³ that the difference between theory and gas-phase experiments on the one hand and matrix isolation experiments on the other hand might be due to the presence of a relatively small and mobile counter cation (Li^+) in the matrix. In 1996, however, Lugez, Thompson, and Jacox⁷ published the results of another matrix isolation study of the IR absorptions of O_3^- where small alkali metal counter cations were not present. Again, they obtained a value of 796 cm^{-1} for the antisymmetric stretch which is much lower than theory or the gas-phase experiment reported in ref.⁶ Further, they put 810 cm^{-1} as an upper bound for the gas-phase fundamental for the antisymmetric stretch of ozonide.

The purpose of the present study is to resolve the discrepancy between matrix isolation studies on the one hand and theory and gas-phase studies on the other. We aim to accomplish this by computing a highly accurate quartic force field and fundamental vibrational frequencies for ozonide. It is well documented now that the CCSD(T) level of theory in conjunction with large one-particle basis sets performs very well in predicting fundamental vibrational frequencies (see refs⁹⁻¹¹ and references therein), and in fact this approach has performed well even for the parent ozone molecule¹². Moreover, this conclusion is as valid for negative ions and radicals as for neutrals, cations, and closed-shell molecules^{13,14}. The theoretical ap-

proach is detailed in the next section followed by results and discussion. The final section contains our conclusions.

COMPUTATIONAL

The CCSD(T)¹⁵ and CASPT2¹⁶⁻¹⁸ electronic structure methods have been used in conjunction with the augmented correlation consistent basis sets^{19,20}. Three basis sets have been used which are designated aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ. The aug-cc-pVQZ basis set is composed of 6s5p4d3f2g contracted basis functions, while the aug-cc-pVTZ and aug-cc-pVDZ basis sets are composed of 5s4p3d2f and 4s3p2d contracted functions, respectively. Only the spherical harmonic components of the d-, f-, and g-type functions were included in the calculations. The CCSD(T) calculations were performed with the restricted open-shell method defined by Watts *et al.*²¹ using the MOLPRO program package²². The CASPT2 calculations were performed with the MOLCAS program package²³. Consistent with previous work³, the CASSCF active space was composed of the 2p-like molecular orbitals leading to a distribution of thirteen electrons among nine orbitals.

Equilibrium geometries were optimized using gradients generated by finite differences of energies. Residual gradients are less than 1×10^{-5} a.u. Force fields were then evaluated by setting up an evenly spaced central difference grid in symmetry internal coordinates about the equilibrium geometry with displacements of one Δ being equal to 0.005 Å for the stretches and 0.005 rad for the angle. The grid required calculation of ten energies for the quadratic force field, including the equilibrium point, and 55 energies for the full quartic field, again including the equilibrium point. The symmetry internal coordinates were defined in the usual way for a C_{2v} triatomic molecule and are given by:

$$S_1(\mathbf{a}_1) = 1/\sqrt{2}(r_1 + r_2) \quad (1)$$

$$S_2(\mathbf{a}_1) = \theta \quad (2)$$

$$S_3(\mathbf{b}_2) = 1/\sqrt{2}(r_1 - r_2). \quad (3)$$

The constants for the full quartic force field, \mathbf{F} , were determined by performing a least squares fit of the energies to the following potential expansion:

$$V = E_0 + 1/2 \sum_{ij} F_{ij} \Delta S_i \Delta S_j + 1/6 \sum_{ijk} F_{ijk} \Delta S_i \Delta S_j \Delta S_k + \\ 1/24 \sum_{ijkl} F_{ijkl} \Delta S_i \Delta S_j \Delta S_k \Delta S_l. \quad (4)$$

The sum of the squared residuals was $1.6 \times 10^{-17} E_h$, showing that the fit was well conditioned. The advantage of a least squares fit procedure is that it eliminates some higher-order contamination (e.g., quartic contamination for the quadratic force constants). Force fields where only the quadratic part or a particular quartic constant was computed were determined using finite difference procedures. We tested the finite difference procedure against the results from the least-squares fit procedure for the full quartic force field and found differences of less than one per cent for the quadratic and cubic constants and less than four per cent for the larger quartic constants, showing that the finite difference procedure was well behaved. Most importantly, for the F_{3333} constant the difference between the finite difference procedure and the least-squares fit was less than one per cent.

For the CASPT2 calculations, the number of significant digits in the energies was not as great as for the CCSD(T) calculations, which necessitated using a least-squares fit procedure for the F_{33} and F_{3333} force constants. This procedure was tested for stability of the resulting constants. The most reliable constants were obtained using nine data points in the fit for F_{33} and F_{3333} , namely the equilibrium energy plus displacements at ± 0.02 , ± 0.04 , ± 0.06 , and ± 0.08 Å. The sum of squared residuals was $2.9 \times 10^{-11} E_h$.

Anharmonic spectroscopic analysis was performed with a modified version of the SPECTRO²⁴ program. Vibrational term values were also computed using an exact variational treatment after transforming the symmetry internal coordinate quartic force field into a Morse-cosine coordinate system (see ref.²⁵). The Morse coordinate was defined as

$$S_{r_1} = 1 - \exp[-\alpha_r(r_1 - r_0)], \quad (5)$$

where $\alpha_r = -f_{rrr}/3f_{rr}$, and f_{rrr} and f_{rr} are the simple internal coordinate force constants (i.e., the symmetry internal coordinate force constants trans-

formed into simple internal coordinates). The cosine coordinate is defined as

$$S_{\Theta} = [\cos(\theta) - \cos(\theta_0)]. \quad (6)$$

The variational calculations were performed with a program developed by Schwenke²⁶.

RESULTS AND DISCUSSION

Equilibrium Geometries and Harmonic Frequencies

Table I contains the equilibrium geometries and harmonic frequencies of O_3^- obtained in the present work. The CASPT2 value is in reasonable agreement with that reported in ref.³, with the bond distance being 0.003 Å longer. Consistent with this observation, the CASPT2 ω_3 harmonic frequency in the present work is 19 cm^{-1} smaller than that calculated previously. These results suggest that the aug-cc-pVTZ and [5s4p3d2f] ANO basis set used previously exhibit only minor differences. The best CCSD(T) equilibrium geometry reported here was determined with the aug-cc-pVQZ basis set. The CCSD(T)/aug-cc-pVQZ equilibrium bond distance is 0.007 Å shorter than the CCSD(T)/aug-cc-pVTZ value, and the corresponding difference in the equilibrium bond angle is only 0.04°. These small differences indicate that the O_3^- equilibrium structure is converged, for our purposes, with

TABLE I
Equilibrium structure (in Å and °) and harmonic frequencies (in cm^{-1}) for O_3^-

	CCSD		CCSD(T)		CASPT2	Expt
	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ	
r_e	1.3395	1.3692	1.3575	1.3503	1.3640	1.34 ± 0.03^a 1.36 ± 0.02^b
θ_e	115.09	114.76	115.05	115.09	115.30	112.6 ± 2.0^a 111.8 ± 2.0^b
$\omega_1(a_1)$		987.1	1027.8	1040.6		
$\omega_2(a_1)$		566.3	583.7	592.3		
$\omega_3(b_2)$	861.0	792.6	862.6	884.7	860.1	

^a Ref.²⁹ The experimental data refer to a vibrationally averaged structure. ^b Ref.⁶

the aug-cc-pVTZ basis set. Note that the difference between the CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ equilibrium geometrical parameters is considerably larger.

Triple excitations have a noticeable effect on the equilibrium bond distance as evidenced by comparison of the CCSD/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ equilibrium structures. This result is consistent with our computed open-shell T_1 diagnostic²⁷ value of 0.038 (computed at the CCSD(T)/aug-cc-pVTZ geometry with the same basis set). The T_1 diagnostic for O_3^- is even larger than it is for O_3 (ref.¹²), 0.025, but it is not outside the range for which CCSD(T) has performed well (for example, see ref.²⁸). Moreover, the agreement between the CCSD(T) and CASPT2 equilibrium geometries and harmonic frequencies suggests that both methods are treating dynamic and non-dynamic electron correlation adequately.

Comparison of the best CCSD(T) and CASPT2 equilibrium structures with the experimental vibrationally averaged structures^{6,29} shows good agreement for the bond distance, but the agreement for the bond angle is not as good being just outside the experimental uncertainties. The uncertainty in the experiments is large, and it may be that the authors of these studies have been overly optimistic in assigning this quantity. As we show later, vibrational averaging increases both the bond distance and bond angle, so this cannot be a factor in the small disagreement for the bond angle. In addition, examination of the bond angles in Table I shows that correlation beyond CCSD has only a small effect on the bond angle, but improvements in the one-particle basis set increase the value. Hence our best value, 115.09° , should be well converged. Based on these observations we feel that the experimental values are somewhat too low.

Examination of the antisymmetric harmonic frequency values, ω_3 , in Table I shows that electron correlation beyond CCSD has little effect on this quantity, with the CCSD, CCSD(T), and CASPT2 values all within 2.5 cm^{-1} of one another. Improvements in the one-particle basis set, on the other hand, cause ω_3 to increase, with the CCSD(T) value being 792.6 , 862.6 , and 884.7 cm^{-1} for the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, respectively. ω_1 and ω_2 exhibit a smaller, but still significant effect due to improvements in the one-particle basis set. Overall, the agreement between the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ harmonic frequencies is as expected and similar to the situation for O_3 (ref.¹²), indicating that the CCSD(T)/aug-cc-pVTZ level of theory is adequate for evaluation of a quartic force field.

Fundamental Frequencies, Force Constants, and Anharmonic Constants

Table II contains the fundamental vibrational frequencies for O_3^- obtained from the CCSD(T)/aug-cc-pVTZ quartic force field. The vibrational frequencies have been obtained using second-order perturbation theory (see ref.³⁰ for asymmetric top formulae) and using exact variational calculations as described in the methods section. We note that the perturbation theory zero-point level includes the E_0 constant³¹. Agreement between the second-order perturbation theory and variational fundamental frequencies is excellent with the largest difference, 8.1 cm^{-1} , occurring for ν_1 . The difference for ν_2 and ν_3 is less than 0.5 cm^{-1} . The difference between perturbation theory and the variational calculation for ν_1 is, in part, probably due to a minor Fermi resonance which occurs, $2\omega_2 \cong \omega_1$. The standard perturbation theory treatment for this resonance (e.g., see ref.³²) changes ν_1 by less than 1 cm^{-1} , but higher-order terms resulting from the better limiting behavior of a Morse coordinate may be responsible. In any case, the overall agreement between perturbation theory and the variational treatment is excellent, demonstrating that our computed fundamental vibrational

TABLE II
Fundamental vibrational frequencies (in cm^{-1}) for O_3^- ^a

	Perturbation theory	Variational	Expt
Zero-point	1255.6	1259.1	
$\omega_1(a_1)$	1027.8	1027.8	
$\omega_2(a_1)$	583.7	583.7	
$\omega_3(b_2)$	862.6	862.6	
$\nu_1(a_1)$	997.7	1005.8	982(30) ^b 975(50) ^c
$\nu_2(a_1)$	572.6	572.1	550(50) ^{b,c}
$\nu_3(b_2)$	941.8	942.2	880(50) ^c
Δ_1	-30.1	-22.0	
Δ_2	-11.1	-11.6	
Δ_3	79.2	79.6	

^a Computed with the CCSD(T)/aug-cc-pVTZ quartic force field. The variational calculation used the force field transformed into Morse-cosine coordinates as described in the text. Δ refers to the difference between the fundamental and harmonic frequencies (i.e., the anharmonic correction). The perturbation theory zero-point level includes the E_0 constant. ^b Ref.⁵

^c Gas-phase IR data from ref.⁶

frequencies are reliable with respect to the solution of the nuclear Schrödinger equation.

The most interesting result in Table II is the fact that ν_3 exhibits a *positive* anharmonic correction. That is, the harmonic frequency is smaller in magnitude than the fundamental frequency, and this correction is not small, being over 79 cm^{-1} . The anharmonic corrections for ν_1 and ν_2 are smaller and entirely consistent with those found for ozone¹² and other similar molecules. The anharmonic correction for ν_3 , however, is very different from that found for ozone. Detailed comparison of the O_3 (ref.¹²) and O_3^- (see Table III) CCSD(T) quartic force fields shows that the main difference lies in the quartic force constant for the antisymmetric stretch, F_{3333} . For ozone this constant is $105.4\text{ aJ}/\text{Å}^4$ while for ozonide anion it is $635.835\text{ aJ}/\text{Å}^4$. This is a very large quartic force constant and gives the potential along the antisymmetric coordinate steep walls as the quartic term dominates all coupling to cubic terms. These results suggest that the gas-phase and matrix environments are noticeably different for the antisymmetric part of the O_3^- potential.

In order to verify the accuracy of the F_{3333} force constant, it was computed at several additional levels of theory, including CCSD/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ, and CASPT2/aug-cc-pVTZ. All the force constants determined in this study are collected in Table III. The CCSD(T)/aug-cc-pVQZ F_{3333} constant is even larger than the CCSD(T)/aug-cc-pVTZ value showing that one-particle basis set improvements will yield a larger constant, not a smaller one. Comparison of the CCSD, CCSD(T), and CASPT2 force constants (all determined with the aug-cc-pVTZ basis set) shows that in contrast to the F_{33} constant, F_{3333} is sensitive to the choice of electron correlation treatment. However, all of the values are much larger than the corresponding O_3 constant. Furthermore, substitution of the CASPT2 F_{33} and F_{3333} constants into the perturbation theory anharmonic analysis still yields a positive anharmonic correction of 42.4 cm^{-1} , and a ν_3 value of 902.5 cm^{-1} . From this analysis it is evident that the anharmonic correction for ν_3 is sensitive to the treatment of electron correlation, but given the high level of theories used here and the fact that we have applied both highly correlated single reference and multireference approaches, it is safe to conclude that the ν_3 anharmonic correction for the free gas-phase O_3^- species is indeed positive. Taking into account the sensitivity of the F_{3333} constant with respect to level of theory, the agreement between the theoretical and experimental^{5,6} fundamental frequencies in Table II is good. We note that positive anharmonic corrections are also known to occur for the antisymmetric stretch of FHF^- , a strongly bound molecular anion³³.

It is interesting to contrast the fundamental frequencies for O_3^- computed in this study with those evaluated in ref.³ In the earlier paper, a CASPT2/[5s4p3d2f] force field beyond quadratic (cubic in some coordinates and quartic in others, but the symmetric stretching coordinate was transformed into a Morse coordinate, giving contributions from higher order force field terms; see ref.³ for a complete description) was computed for the $Li^+O_3^-$ complex and then the O_3^- part of the potential was used in a variational calculation of the fundamental frequencies. In this case, the antisymmetric stretch was found to exhibit a negative anharmonicity, as

TABLE III
Quadratic, cubic, and quartic force constants for O_3^- ^a

Force contant	CCSD		CCSD(T)		CASPT2
	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVTZ
F_{11}		5.28821	5.79551	5.94949	
F_{12}		0.21939	0.23957	0.25076	
F_{22}		1.64905	1.70381	1.73404	
F_{33}	2.88201	2.44766	2.89333	3.04323	2.87212
F_{111}			-26.2024		
F_{112}			-1.6579		
F_{122}			-3.6547		
F_{222}			-2.7639		
F_{133}			-23.9014		
F_{233}			-0.6747		
F_{1111}			111.478		
F_{1112}			8.152		
F_{1122}			7.198		
F_{1222}			6.889		
F_{2222}			8.736		
F_{1133}			85.408		
F_{1233}			9.692		
F_{2233}			-3.822		
F_{3333}	394.86		635.835	674.73	466.794

^a Constants have an energy unit of aJ and length units of Å and rad. The symmetry internal coordinates are defined in Eqs (1) through (3). Constants defined according to Eq. (4).

was the symmetric stretch. The agreement between the present fundamentals and those computed in ref.³ is very good except for the antisymmetric stretch. This comparison lends further support to our assertion that the matrix environment is significantly different than the gas-phase environment for O_3^- . In summary, CASPT2 calculations on free O_3^- yield a positive anharmonic correction for the antisymmetric stretch, but CASPT2 calculations in the presence of a Li^+ counter cation yield a negative anharmonic correction for the antisymmetric stretch. The potential along the antisymmetric stretch coordinate is clearly sensitive to the external environment.

For completeness, the CCSD(T)/aug-cc-pVTZ anharmonic constants and vibrationally averaged geometry are listed in Table IV.

Fundamental Vibrational Frequencies for Isotopomers

Table V presents the harmonic and fundamental frequencies for all possible ^{16}O and ^{18}O isotopomers of O_3^- determined using second-order perturbation theory and the CCSD(T)/aug-cc-pVTZ quartic force field. These are compared with the isotopic shifts observed for ν_3 in a recent matrix isolation experiment⁷. Regarding the antisymmetric stretch, the theoretical isotopic shifts for the fundamentals are larger than for the harmonic frequencies due to the positive anharmonic correction. Comparison of the theoretical harmonic and fundamental isotopic shifts with those determined in the recent neon matrix studies⁷ shows reasonable agreement, es-

TABLE IV
Vibrationally averaged structure and anharmonic constants (in cm^{-1}) for O_3^- ^a

	CCSD(T)
r_g	1.3656
θ_g	115.11
X_{11}	-3.655
X_{12}	-5.069
X_{13}	-40.616
X_{22}	-0.941
X_{23}	-13.289
X_{33}	53.112

^a Bond length in Å and bond angle in °. Computed with the aug-cc-pVTZ basis set and quartic force field.

pecially for the harmonic isotopic shifts. This agreement confirms the assignment of O_3^- , but the disagreement in the absolute frequencies suggests that the matrix environment and gas-phase environment are different for O_3^- . It is hoped that the data in Table V will be useful in the interpretation of future gas-phase experiments on different isotopomers of ozonide anion.

CONCLUSIONS

A highly accurate CCSD(T)/aug-cc-pVTZ quartic force field and fundamental vibrational frequencies have been computed for the ozonide anion. Equilibrium structures and certain potential force constants have also been evaluated at the CCSD and CASPT2 levels of theory in order to assess the reliability of the CCSD(T) fundamental frequencies.

TABLE V
Harmonic and fundamental frequencies for the ^{16}O and ^{18}O isotopomers^a

	$^{16}\text{O}_3$	$^{16}\text{O}^{18}\text{O}^{16}\text{O}$	$^{16}\text{O}^{16}\text{O}^{18}\text{O}$	$^{16}\text{O}^{18}\text{O}^{18}\text{O}$	$^{18}\text{O}^{16}\text{O}^{18}\text{O}$	$^{18}\text{O}_3$
$\omega_1(\text{a}_1)$	1027.8	999.0	1014.3	984.8	999.1	968.9
$\omega_2(\text{a}_1)$	583.7	577.8	569.6	564.0	555.4	550.2
$\omega_3(\text{b}_2)$	862.6	833.9	851.8	822.7	842.5	813.1
$\Delta\omega_1(\text{a}_1)$	0	-28.8	-13.5	-43.0	-28.7	-58.9
$\Delta\omega_2(\text{a}_1)$	0	-5.9	-14.1	-19.7	-28.3	-33.5
$\Delta\omega_3(\text{b}_2)$	0	-28.7	-10.8	-39.9	-20.1	-49.5
$\nu_1(\text{a}_1)$	997.7	970.2	985.6	957.6	970.9	942.1
$\nu_2(\text{a}_1)$	572.6	567.2	559.0	553.9	545.1	540.4
$\nu_3(\text{b}_2)$	941.8	907.8	928.8	894.3	918.3	883.6
$\Delta\nu_1(\text{a}_1)$	0	-27.5	-12.1	-40.1	-26.8	-55.6
$\Delta\nu_2(\text{a}_1)$	0	-5.4	-13.6	-18.7	-27.5	-32.2
$\Delta\nu_3(\text{b}_2)$	0	-34.0	-13.0	-47.5	-23.5	-58.2
Expt ^b ν_3	796.3	770.5	786.1	759.5	778.3	751.9
Expt ^b $\Delta\nu_3$	0	-25.8	-10.2	-36.8	-18.0	-44.4

^a Computed at the CCSD(T)/aug-cc-pVTZ level of theory using second-order perturbation theory for the vibrational analysis. Labeling of modes refers to the parent isotopomer. The Δ rows refer to the shift from the parent $^{16}\text{O}_3$ isotopomer. ^b Ne matrix isolation results from ref.⁷ for the antisymmetric stretch, ν_3 .

Agreement between theory and gas-phase experiments for the bond distance of O_3^- is good, although for the bond angle it appears that the low-resolution experiments have been interpreted to give a value that is too small. Our computed fundamentals are in agreement with gas-phase experiments and in particular, they disagree with matrix isolation experiments for the antisymmetric stretch. The theoretical fundamental for the antisymmetric stretch exhibits an unusual positive anharmonicity. The results of this study, taken with the experimental gas-phase study⁶, lead us to conclude that there is a very large matrix shift for this band. Support for this assertion is given by the fact that the CASPT2 ν_3 fundamental exhibits positive anharmonicity for the free gas-phase species, but the usual negative anharmonicity when a Li^+ counter ion is present. In other words, the antisymmetric part of the O_3^- potential surface is shown to be very sensitive to the external environment. It is hoped that the theoretical data presented herein will be useful in the interpretation of future high-resolution gas-phase experiments.

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REFERENCES

1. Garner M. C., Sherwood C. R., Hanold K. A., Continetti R. E.: *Chem. Phys. Lett.* **1996**, *248*, 20.
2. Cui Q., Morokuma K.: *J. Chem. Phys.* **1998**, *108*, 7684.
3. Borowski P., Roos S. B. O., Racine C., Lee T. J., Carter S.: *J. Chem. Phys.* **1995**, *103*, 266.
4. Matejcik S., Cicman P., Kiendler A., Skalny J. D., Illenberger E., Stamatovic A., Märk T. D.: *Chem. Phys. Lett.* **1996**, *261*, 437.
5. Novick S. E., Engelking P. C., Jones P. L., Futrell J. H., Lineberger W. C.: *J. Chem. Phys.* **1979**, *70*, 2652.
6. Arnold D. W., Xu C., Kim E. H., Neumark D. M.: *J. Chem. Phys.* **1994**, *101*, 912.
7. Laguez C. L., Thompson W. E., Jacox M. E.: *J. Chem. Phys.* **1996**, *105*, 2153.
8. Jacox M. E.: data compiled for O_3^- at <http://webbook.nist.gov>.
9. Lee T. J., Scuseria G. E. in: *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy* (S. R. Langhoff, Ed.), p. 47. Kluwer, Dordrecht 1995.
10. Martin J. M. L., Lee T. J., Taylor P. R.: *J. Chem. Phys.* **1998**, *108*, 676.
11. Lee T. J., Martin J. M. L.: *Chem. Phys. Lett.* **2002**, *357*, 319.
12. Lee T. J., Scuseria G. E.: *J. Chem. Phys.* **1990**, *93*, 489.
13. Lee T. J., Dateo C. E.: *J. Chem. Phys.* **1997**, *107*, 10373.
14. Lee T. J., Dateo C. E.: *Spectrochim. Acta, Part A* **1999**, *55*, 739.
15. Raghavachari K., Trucks G. W., Pople J. A., Head-Gordon M.: *Chem. Phys. Lett.* **1989**, *157*, 479.

16. Andersson K., Malmqvist P.-Å., Roos B. O., Sadlej A. J., Wolinski K.: *J. Phys. Chem.* **1990**, *94*, 5483.
17. Andersson K., Malmqvist P.-Å., Roos B. O.: *J. Chem. Phys.* **1992**, *96*, 1218.
18. Andersson K., Roos B. O. in: *Modern Electron Structure Theory* (R. Yarkony, Ed.), Vol. 1. World Scientific, Singapore 1995.
19. Dunning T. H.: *J. Chem. Phys.* **1989**, *90*, 1007.
20. Kendall R. A., Dunning T. H., Harrison R. J.: *J. Chem. Phys.* **1992**, *96*, 6796.
21. Watts J. D., Gauss J., Bartlett R. J.: *J. Chem. Phys.* **1993**, *98*, 8718.
22. Werner H.-J., Knowles P. J. (with contributions from Almlöf J., Amos R. D., Deegan M. J. O., Elbert S. T., Hampel C., Meyer W., Peterson K., Pitzer R., Stone A. J., Taylor P. R.): *MOLPRO 96, A Package of ab initio Programs*, 1996.
23. Andersson K., Blomberg M. R. A., Fülscher M. P., Kellö V., Lindh R., Malmqvist P.-Å., Noga J., Olsen J., Roos B. O., Sadlej A. J., Siegbahn P. E. M., Urban M., Widmark P.-O.: *MOLCAS, A Suite of Quantum Chemistry Programs*. University of Lund, Lund 1998.
24. Gaw J. F., Willetts A., Green W. H., Handy N. C.: *SPECTRO*, Version 1.0. University of Cambridge, Cambridge 1989.
25. Dateo C. E., Lee T. J., Schwenke D. W.: *J. Chem. Phys.* **1994**, *101*, 5853.
26. Schwenke D. W.: *Comput. Phys. Commun.* **1992**, *70*, 1.
27. Jayatilaka D., Lee T. J.: *J. Chem. Phys.* **1993**, *98*, 9734.
28. Martin J. M. L., Lee T. J., Scuseria G. E., Taylor P. R.: *J. Chem. Phys.* **1992**, *97*, 6549.
29. Wang L. J., Woo S. B., Helmy E. M.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1987**, *35*, 759.
30. Mills I. M. in: *Molecular Spectroscopy – Modern Research* (K. N. Rao and C. W. Mathews, Eds), p. 115. Academic, London 1972.
31. Truhlar D. G., Isaacson A. D.: *J. Chem. Phys.* **1991**, *94*, 357.
32. Martin J. M. L., Lee T. J., Taylor P. R., Francois J.-P.: *J. Chem. Phys.* **1995**, *103*, 2589.
33. Janssen C. L., Allen W. D., Schaefer H. F., Bowman J. M.: *Chem. Phys. Lett.* **1986**, *131*, 352.