NO_3ラジカルの振動波数と強度のパッケージによる計算

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Calculation of the vibrational frequencies and intensities for the NO_3 radical with program packages

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The infrared frequency and intensity of the ν_3 degenerate N-O stretching fundamental vibration in the ground electronic X^2A_2' state of the NO_3 radical are a debated issue. The initial assignment of the ν_3 fundamental was for the observed strongest infrared band at 1492 cm^{-1} with some anomalies on the isotopic shift and the Coriolis coupling constant.[1] Calculations with the model Hamiltonian approach by Stanton[2] predicted a very weak ν_3 fundamental near 1069 cm^{-1} and reassigned the 1492 cm^{-1} band as the $\nu_3+\nu_4$ combination for NO_3. The latter point has been supported by the analysis of the matrix spectroscopic observation[3] around 1492 cm^{-1} for various isotopic species of NO_3 and the analysis of the FTIR spectroscopic observation[4] around 1127 cm^{-1} for the hot $\nu_3+\nu_4-\nu_4$ band. The LIF observation[5] of the B^2E'-X^2A_2' transition revealed a 1056 cm^{-1} band for $^{14}NO_3$ and a 1039 cm^{-1} band for $^{15}NO_3$, which may be attributed to the expected ν_3 fundamental in the ground electronic X^2A_2' state,[6] but was also argued for other possible assignments.[7] A recent calculation[8] using the code MULTIMODE showed a similar result as Stanton's calculation. In the present study, we show that the low frequency and weak IR intensity for the ν_3 fundamental of NO_3 can be reproduced simply with two program packages, Gaussian09 and Molpro 2012.

We first tested the closed shell species with the D_{3h} structure: BF_3, SO_3, and NO_3^- to compare with the calculation for NO_3, as shown in Table I. The low level MP3 (third-order Moller-Plesset perturbation theory) method with a small pvdz basis set gave reasonable harmonic vibrational frequencies of all the modes for BF_3, SO_3, NO_3^-, and even for the open shell CH_3 radical when compared with the observed ones, but the MP3 result for NO_3 was too high for ν_3 and ν_4 even with larger basis sets. When the DFT calculation with a B3LYP/pvdz level was applied, ν_3 and ν_4 dropped to less than half for NO_3, but there were little changes on other closed shell species. In the B3LYP calculations

Table I. Comparison of the calculated vibrational wavenumbers (in cm^{-1}) with the experimental ones (numbers in the brackets are infrared intensities in km/mole)

	BF_3				NO_3^-				NO_3			
	MP3	B3LYP	CCSD	Exp.	MP3	B3LYP	CCSD	Exp.	MP3	B3LYP	CCSD	Exp.
ν_1	885 (0)	866 (0)	874 (0)	888	1151 (0)	1074 (0)	1105 (0)	1062	1228 (0)	1140 (0)	1169 (0)	1060
ν_2	725 (115)	689 (89)	717 (109)	691	897 (32)	849 (26)	884 (32)	763	834 (19)	801 (16)	822 (17)	762
ν_3	1493 (433)	1457 (381)	1478 (417)	1454	1575 (608)	1461 (456)	1508 (538)	1350	2446 (3449)	1147 (0.03)	1282 (11)	
ν_4	490 (14)	473 (11)	486 (14)	479	746 (0.6)	714 (1)	731 (0.7)		754 (16)	239 (15)	394 (4)	365

with various basis sets up to avqz, the vibrational frequency of the ν_3 fundamental was given around 1100 cm^{-1}, and the infrared intensity of the ν_3 fundamental was given as less than 1/20 for the ν_2 or ν_4 fundamentals. With the coupled cluster methods at the CCSD, QCISD, and CCSD(T) levels, there were no significant changes on the vibrational frequencies of all the modes for all the species, but the QCISD method gave slightly stronger and the CCSD method gave 50 times stronger infrared intensity for the ν_3 fundamental (the CCSD(T) method could not calculate the infrared intensity). In conclusion, the calculations with the DFT B3LYP method and the coupled cluster methods gave the similar harmonic vibrational frequencies for the fundamentals as the previous model calculations[1,8] including the weak ν_3 fundamental of NO_3 near 1100 cm^{-1}.

We also calculated the Raman intensities for these species with the B3LYP method. The interesting results of the calculation showed that (Fig. 1), although the infrared intensity for the ν_3 fundamental of NO_3 is much weaker than the strongest ν_3 fundamental for the other closed shell D_{3h} species, the Raman intensity for the ν_3 fundamental of NO_3 is over 100 times stronger than the one for the others. Therefore, observing the Raman spectrum (or four-wave mixing spectrum with the similar selection rules) of NO_3 may be the best way to identify the ν_3 fundamental of NO_3.

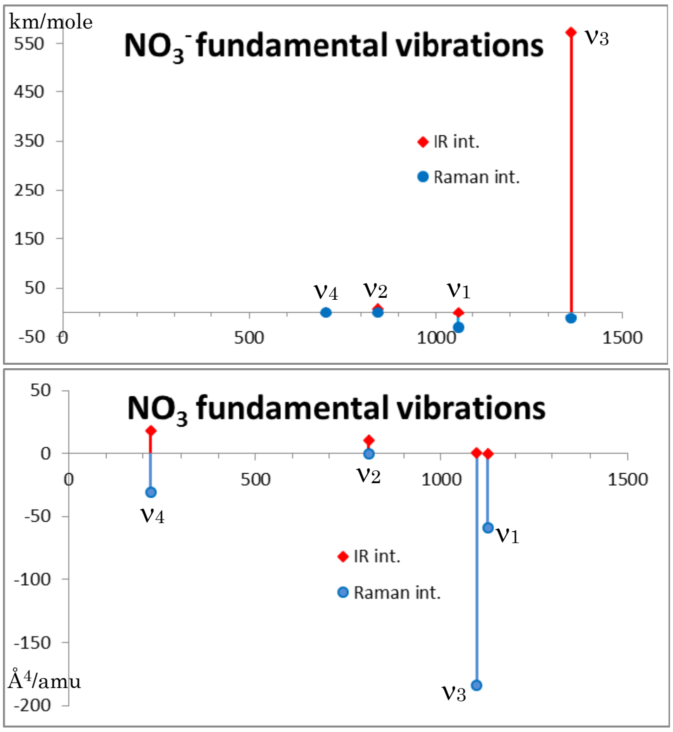

Fig 1. Calculated infrared intensities and Raman scattering activities for NO_3^- and NO_3

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