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## Journal of Molecular Spectroscopy

journal homepage: [www.elsevier.com/locate/jms](http://www.elsevier.com/locate/jms)Gas-phase infrared spectrum of methyl nitrate<sup>☆</sup>John F. Stanton<sup>a,\*</sup>, Bradley A. Flowers<sup>b</sup>, Devin A. Matthews<sup>a</sup>, Asa F. Ware<sup>b</sup>, G. Barney Ellison<sup>b</sup><sup>a</sup> Institute for Theoretical Chemistry, University of Texas at Austin, Mail Stop A5300, Austin, TX 78712, USA<sup>b</sup> Department of Chemistry, University of Colorado, Boulder, CO 80302, USA

## ARTICLE INFO

## Article history:

Received 5 February 2008

In revised form 26 March 2008

Available online 11 April 2008

## Keywords:

Gas-phase  
Infrared  
Spectrum  
Methyl  
Nitrate  
Fundamental

## ABSTRACT

The infrared spectrum of methyl nitrate has been reinvestigated. Analysis of the 0.125 cm<sup>-1</sup> room temperature spectrum has been carried out with the assistance of high-level *ab initio* calculations using coupled-cluster theory. Use of second-order vibrational perturbation theory (VPT2), with allowances—when necessary—for resonances has permitted the complete assignment of all fundamental vibrational modes in this molecule. A few errors in previous assignments are corrected (notably the CH stretching modes that are now assigned as  $\nu_1 = 3034.1$  cm<sup>-1</sup>;  $\nu_2 = 2961.5$  cm<sup>-1</sup>, and  $\nu_{13} = 3014.5$  cm<sup>-1</sup> and the methyl deformation  $\nu_{15}$ , assigned to 1155.7 cm<sup>-1</sup>), and the work also presents a highly accurate empirically adjusted force field that reproduces all fundamental frequencies to within 0.1 cm<sup>-1</sup>. This Hamiltonian should be accurate enough to predict two- and three-quantum transitions to within a few cm<sup>-1</sup>. The remaining fundamental frequencies (in cm<sup>-1</sup>) are  $\nu_4 = 1667.0$ ;  $\nu_5 = 1431.8$ ;  $\nu_6 = 1291.2$ ;  $\nu_7 = 1177.9$ ;  $\nu_8 = 1018.5$ ;  $\nu_9 = 855.4$ ;  $\nu_{10} = 658.3$ ;  $\nu_{11} = 571.0$ ;  $\nu_{12} = 344.2$ ;  $\nu_{14} = 1444.7$ ;  $\nu_{16} = 760.6$ ;  $\nu_{17} = 204.5$ ; and  $\nu_{18} = 133.7$ .

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## 1. Introduction

Complete vibrational assignments of the fundamental modes in relatively complex polyatomic molecules can be a formidable task, especially if the molecule has little or no symmetry and the inertial axes do not coincide with rotational symmetry axes. While it has been appreciated for decades that *ab initio*-quantum chemistry provides valuable information that can aid in the assignment of infrared and Raman spectra [1], the usual approach—using harmonic frequencies to guide the search for specific features and employment of the associated theoretical intensities to distinguish between candidates when the choice of the fundamental is ambiguous—can go only so far. It is, for example, of little utility in the assignment of overtone and combination levels, analyzing resonances of the Fermi and Darling–Dennison variety, and in helping to assign very weak fundamentals in regions of the spectrum where the density of states is high enough to ensure that there are several features in the vicinity of any candidate peak. To be sure, the work of some quantum chemists—notably the Handy [2] and Schaefer [3] groups—has helped the field move beyond the harmonic approximation, and the tools based on their pioneering work can (and have) solve(d) the problems alluded to above.

The purpose of this paper is to illustrate an iterative procedure that we have been using in recent years to assign infrared spectra.

A fruitful area of our present research deals with the identification of radicals and other reactive intermediates, usually in cryogenic matrices. The spectra are often complicated, congested by the presence of other compounds generated in the process of deposition and/or unavoidable impurities in the sample. In general, they are sufficiently difficult to assign that the standard computational approach based on the harmonic approximation is of limited utility, and more sophisticated methods are needed. Our choice has been to use second-order vibrational perturbation theory (VPT2) [4] in conjunction with anharmonic force fields calculated with the coupled-cluster singles and doubles approximation [5], as augmented by the usual non-iterative treatment of triple excitations [CCSD(T)] [6]. In recent years, there have been indications that the atomic natural orbital (ANO) basis sets developed two decades ago by Almlöf and Taylor [7] provide force fields that are superior to those obtained with comparably sized correlation-consistent basis sets [8] that have become the *de facto* standard in the community. Indeed, using an ANO basis set essentially the same size as the cc-pVTZ basis (ANO1), fundamental frequencies evaluated with VPT2 are usually within 10 cm<sup>-1</sup> of gas-phase level positions [9]. Going to the ANO set that is the same size as cc-pVQZ (ANO2), the situation improves yet further [10]. Indeed, such calculations were instrumental in our assignment of the infrared spectrum of matrix-isolated *cis-cis* HOONO [11], and the propargyl radical [12].

Although we have efficient programs for the calculation of analytic second derivatives and have in fact parallelized the approach in the last year [13], calculations of the sort alluded to above can be quite costly for larger polyatomic molecules. The question that arises is the following: is it possible to make shortcuts in the

<sup>☆</sup> Dedicated to our colleagues Herb Pickett and Ed Cohen, in commemoration of their achievements in molecular spectroscopy.

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theoretical methodology without losing so much accuracy that the ability to assign spectra is significantly compromised? This issue will be tacitly addressed in this paper, where we make use of a smaller basis set—designated as ANO0—which is the same size as the (rather small) cc-pVDZ basis. For the practical purpose of using theory to guide assignments, two central questions must first be answered. First, how well does the ANO0 basis set work in predicting the exact (gas-phase) position of vibrational levels in polyatomic molecules? Second, since most of our work on reactive systems is done in argon matrices, what are the magnitude of the shifts due to the matrix environment? To answer either question, the position of vibrational levels in the gas-phase need to be known.

The purpose of this paper is to use the ANO0 basis set in conjunction with CCSD(T) to guide the assignment of a polyatomic molecule. To this end, we have chosen methyl nitrate ( $\text{CH}_3\text{ONO}_2$ ), which has eight atoms,  $C_s$  symmetry, and 18 fundamental vibrational modes. This molecule has been chosen since it is similar to others being studied by the authors: peroxyxynitrites ( $\text{ROONO}$ ) and related molecules, as well as nitroalkanes [14]. Our intention is to document the general approach that we follow to assign spectra. The methyl nitrate molecule provides an excellent system for this illustration.

Methyl nitrate is the simplest organic nitrate. Its rotational spectrum has been measured and its structure is known [15] (see Fig. 1). The molecule has  $C_s$  symmetry, and the vibrational modes transform as  $\Gamma_{\text{vib}} = 12a' + 6a''$ . The methyl torsional barrier has been measured to be  $V_3(\text{CH}_3\text{-ONO}_2) = 980 \pm 40 \text{ cm}^{-1}$  and the nitrate barrier  $V_2(\text{CH}_3\text{ONO}_2)$  is  $2650 \pm 75 \text{ cm}^{-1}$ . It should be noted that some, although surprisingly little, work has been reported previously on the infrared spectrum of gas-phase methyl nitrate. The first was a low-resolution study by Brand and Cowthen in 1955 [16], and the second was a force field study reported the following decade [17]. Additionally, Durig has carried out a far-infrared study of  $\text{CH}_3\text{ONO}_2$ , and has successfully assigned the two lowest-fre-

quency torsional modes,  $\nu_{17}$  and  $\nu_{18}$  [18], information that we use in the present research. The assignment made in this research will be compared to those of the previous works towards the end of this paper.

## 2. Experimental

Methyl nitrate was synthesized by esterifying nitric acid with methanol in excess sulfuric acid [19]. The purity of  $\text{CH}_3\text{ONO}_2$  used in this study was confirmed by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. At room temperature, the sample vial containing  $\text{CH}_3\text{ONO}_2$  was opened and 25 torr of vapor was released into a static IR cell with CsI windows. The length of the cell was 9.8 cm. All features of the  $\text{CH}_3\text{ONO}_2$  spectrum were found to have a direct linear dependence on the pressure input to the static cell and the pressure in the sample cell was observed to be constant over the course of the scan. The spectrum discussed in this paper was taken at  $0.125 \text{ cm}^{-1}$  resolution between 400 and  $6000 \text{ cm}^{-1}$  using a Hg/Cd/Telluride (MCT-A) detector in a Nicolet Magna FTIR spectrometer. Absorption bands from  $\text{CO}_2$  and water are from ambient laboratory air, not the gas inlet to the sample cell.

## 3. Computational

The information needed in VPT2 comprises the quadratic, cubic and most quartic force constants (all but those having four different indices [20]) in the dimensionless normal coordinate representation, the Coriolis zeta matrices, and the first, second and third derivatives of the dipole moment, the latter excluding terms with three different indices [10]. All of this information was calculated for methyl nitrate using the ANO0 basis set at the CCSD(T) level. Analytic second derivative techniques [21] were used, following the general strategy outlined in Ref. [22] with the MAB version of the ACES II program system [23]. The five 1s core orbitals on non-hydrogen atoms were excluded from the correlation treatment,

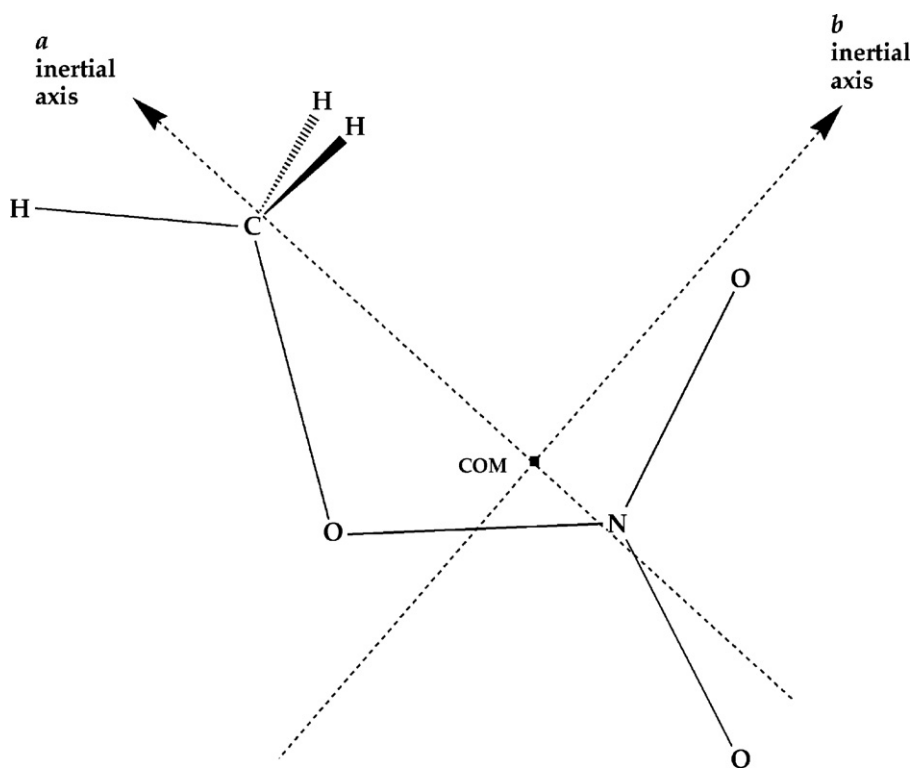


Fig. 1. The geometry for the  $\text{CH}_3\text{ONO}_2$  molecule based on Ref. [15].

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