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Vibrational spectra and structural parameters of some XNCO and XOCN (X = H, F, Cl, Br) molecules

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ABSTRACT

Ab initio calculations with full electron correlation by the perturbation method to second order and hybrid density functional theory calculations by the B3LYP method utilizing the 6-31G(d), 6-311+G(d,p), and 6-311+G(2d,2p) basis sets have been carried out for the XNCO and XOCN (X = H, F, Cl, Br) molecules. From these calculations, force constants, vibrational frequencies, infrared intensities, Raman activities, depolarization ratios, and structural parameters have been determined and compared to the experimental quantities when available. By combining previously reported rotational constants for HNCO, ClNCO and BrNCO with the *ab initio* MP2/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The r_0 values for BrNCO are: r(Br—N) = 1.857(5); r(N=C) = 1.228(5); r(C=O) = 1.161(5) Å; BrNC = 117.5(5) and NCO = 172.3(5)°. For ClNCO the determined r_0 parameters are in excellent agreement with the previously determine r_s values, whereas those for HNCO the HNC angle is larger with a value of 126.3(5)° compared to the previous reported value of 123.9(17)°. However, considering the relatively large uncertainty in the value given initially the two results are in near agreement. Structural parameters are also estimated for FNCO and XOCN (X = H, F, Cl, Br). The centrifugal distortion constants have been calculated and are compared to the experimentally (XNCO: X = H, Cl, Br) determined values. Predicted values for the barriers of linearity are given for both the XNCO (X = H, F, Cl, Br) molecules and the results were compared to the corresponding isothiocyanate molecules. The predicted frequencies for the fundamentals of the XNCO molecules compare favorably to the experimental values but some of the predicted intensities differ significantly from those in the observed spectra. The two OCN bends for HOCN have been assigned and the frequencies for the two corresponding fundamentals of DOCN are predicted.

1. Introduction

Recently we initiated some spectroscopy studies supported by *ab initio* and density functional theory calculations of some YN_3 [1,2] and YNCS [3–6] molecules where Y was an organic, silyl, germyl or halogen moiety. Since the YNC angle is relatively large or in some cases linear, the NCS moiety has nearly free or free rotation which significantly effects the vibrational and rotational spectra. For example, the barrier to internal rotation for methylisothiocyanate (CH_3NCS) is ~3 cm^{-1} which results in essentially free rotation of the methyl group with the degeneracy of the two NCS bends [5]. In the infrared spectrum of the gas phase, two of the antisymmetric (pseudodegenerate) vibrations of the CH_3 groups have resolvable fine structure where the spacing is 9.8 cm^{-1} for the stretch and 13.8 cm^{-1} for the deformation where the spacing is determined by the ζ values for these normal modes for the CH_3NCS molecule [5]. Also the two NCS bends give a very strong broad infrared band in the gas and liquid along with a much weaker lower frequency band. In the infrared spectrum of the solid the very broad band essentially disappears leaving the single lower frequency band which may indicate a linear CNCS. This very low C—NCS torsional barrier for the methyl compound is also found for the corresponding ethyl compound [6] which results in a single stable *cis* conformer (CH_3 group *cis* to the NCS moiety) for this molecule which is at variance with the predictions from *ab initio* calculations up to TZVP [7]. Because of these large amplitude vibrations for these types of molecules, it has frequently been difficult to assign their microwave spectra from which rotational constants can be obtained for determining the r_0 or r_s structural parameters. However, it is frequently possible to combine a limited number of experimentally determined rotational constants with *ab initio* predicted structural parameters to obtain r_0 structural parameters that have significantly smaller uncertainties than those obtain from the microwave spectral data [8]. Such results have been obtained for HN_3 [1], CH_3N_3 [2], HNCS [3] and GeH_3NCS [5].

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Since the XNC (X = H, CH_3) for the isocyanate is significantly smaller [9,10] than the corresponding angles for the XNCS [3,5] molecules, it is expected that the barrier to linearity will be much larger for the corresponding isocyanates. Also the N=C distances may be significantly different between isocyanate and the corresponding isothiocyanate molecules. Therefore, as a continuation of these spectroscopic and theoretical investigations we have carried out similar studies of XNCO and XOCN where X = H, F, Cl, and Br for comparison to the corresponding isothiocyanate (NCS) molecules. The results of these theoretical studies along with comparisons to the experimental data when appropriate are reported herein.

2. Theoretical calculations

In order to provide vibrational frequencies with both infrared and Raman intensities and optimized geometries, *ab initio* calculations were carried out by using the Gaussian-03 program [11] at both the restricted Hartree–Fock (RHF) level and by the perturbation method to second order (MP2) [12] with full electron correlation. Three basis sets, 6-31G(d), 6-311+G(d) and 6-311+G(2d) have been utilized. Hybrid density functional theory (DFT) calculations have also been carried out by the B3LYP method utilizing the 6-311+G(d) basis set. Frequencies for the fundamentals have been predicted for the XNCO (X = H, F, Cl, Br) molecules, along with the predicted infrared and Raman activities and these data are listed in Table 1. Similar data have also been obtained for the corresponding XOCN (X = H, F, Cl, Br) molecules which are listed in Table 2. The predicted values are compared to the experimental values when they are available.

In order to obtain a complete description of the molecular motion involved in the normal modes, the force field in Cartesian coordinates was calculated with the 6-31G(d) and 6-311+G(d) basis sets at the MP2 level as well as with 6-311+G(d) basis set from the hybrid DFT calculations by B3LYP method. The internal coordinates were the X—N, N=C, and C=O distances, the XNC and NCO angle bends, and the out-of-plane angle bend for the isocyanates and X—O, O—C and C≡N distances, the XOC and OCN bends, and the out-of-plane bend for the cyanates. The symmetry coordinates were these internal coordinates individually except we also combined the C=O and N=C coordinates for antisymmetric and symmetric stretches for the isocyanates. The **B** matrix was used to convert the *ab initio* force field in Cartesian coordinates to a force field in internal coordinates [13]. The frequencies from the MP2/6-31G(d) calculation were also calculated by utilizing a set of scaling factors of 0.88 for the N—H (N—D) stretches, 0.9 for HNC (DNC) bends, and 1.0 for all other coordinates with the geometric average for the off-diagonal terms for HNCO. Except for the acid the potential energy distributions (PEDs) are expressed in terms of the symmetry coordinates where S_1 is NCO antisymmetric stretch, S_2 is the NCO symmetric stretch, S_3 is the X—N stretch, S_4 is the NCO bend, S_5 is the XNC bend and S_6 is out-of-plane bend; these potential energy distributions are listed in Table 1. For the acid, S_1 is N—H (N—D) stretch, S_2 is NCO antisymmetric stretch, S_3 is the NCO symmetric stretch, S_4 is HNC (DNC) bend, S_5 is NCO bend and S_6 is the out-of-plane bend. The pure *ab initio* frequencies, infrared intensities, Raman scattering activities, along with the B3LYP/6-311+G(d) calculation results are also given in Table 1.

In order to show the differences in the predicted and observed spectra for the fluoro-, chloro- and bromo-isocyanates as well as the difference in the infrared and Raman spectra for the hydrogen and halocyanates, we calculated the theoretical infrared and Raman spectra. The calculated frequencies, infrared intensities, and Raman scattering activities were obtained from both the *ab initio* and hybrid DFT calculations. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the *ab initio* calculation and transformed to the normal coordinates by $(\partial\mu_u/\partial Q_i) = [\Sigma(\partial\mu_u/\partial X_j)]L_{ij}$, where Q_i is the i^{th} Cartesian displacement coordinate, L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by: $I_i = [(N\pi)/(3c^2)]\ [(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$.

In Figs. 1–3, the predicted infrared spectra from the MP2(full)/6-31G(d) calculations are shown for each XNCO (X = F, Cl, Br) molecule. For comparison the experimental infrared spectra of the gas or in a matrix are also shown. The observed ones show some slight differences from the predicted ones for these molecules. For the other molecules (HNCO and DNCO Fig. 4) mainly the predicted infrared and Raman spectra are shown as well as for the cyanates XOCN (X = H, D, F, Cl, and Br) since intensity data are not available except for a small portion of the infrared spectra of HNCO and HOCN.

The evaluation of the Raman activity by using the analytical gradient method has been developed [14,15]. Where the activity, S_j, can be expressed as: $S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$ and g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. The Raman scattering cross sections, which are proportional to the Raman intensities, can be calculated from the scattering activities [16,17]. To obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1-\rho_j)/(1+\rho_j)$, where ρ_j is the depolarization ratio of the j^{th} normal mode. The Raman scattering cross sections and the calculated frequencies were used together with the Lorentzian function to obtain the calculated spectrum. The predicted Raman spectrum for the individual molecules is shown below the infrared spectrum but only the experimental one for BrNCO is conveniently available for comparison.

3. Vibrational spectra and structural parameters

The predicted vibrational spectra for the XNCO (X = H, D, F, Cl, Br) molecules are shown in Figs. 1–4 and it should be noted that in general there are significant differences in the predicted intensities of the lower frequency bending modes of the infrared spectra and those in the Raman spectra. For example, with BrNCO, the ν_4 fundamental is barely observable in the infrared spectrum but it is the strongest Raman band. Similarly the ν_6 mode is extremely weak in the Raman spectrum but the third strongest band in the infrared spectrum. Some similar differences are also predicted for the other XNCO molecules (X = F and Cl). Thus, these data could be of significant importance for any future Raman studies of the other halocyanates. However, infrared and Raman data as well as experimental structural data are available for isocyanic acid.

3.1. Isocyanic acid (HNCO and DNCO)

The predicted infrared spectrum of HNCO from scaled MP2/6-31G(d) calculations is shown in Fig. 4B and that for DNCO in 4D, and the corresponding Raman spectra are shown in 4C and 4E, respectively. The predicted intensities for ν_2 in the Raman spectra makes them almost unobservable compared to the other Raman line intensities whereas the corresponding symmetric NCO stretch (ν_3) is the most intense Raman line with the corresponding infrared band extremely weak as might be expected from a comparison of these corresponding modes of CO_2. Because of this exceedingly small intensity, this mode was misassigned in the early infrared investigation [18] with a frequency of 1527 cm^{-1}. The question concerning the correct assignment for ν_3 should not have occurred