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Acetonitrile N-Oxide. Infrared Spectrum and Symmetry Force Constants[1]

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Abstract: The vibrational frequencies for acetonitrile N-oxide have been observed in the 4000-200-cm^{-1} region of the spectrum, and assignments of these frequencies to the normal modes of vibration have been made. Symmetry force constants have been calculated using a hybrid orbital force field. The frequencies associated with the methyl group, and the corresponding force constants, have essentially the same values as in other molecules of C_{3v} symmetry containing a methyl group. The CC stretching frequency appears at 778 cm^{-1}, the CN stretching frequency at 2315 cm^{-1}, and the NO stretching frequency at 1319 cm^{-1}. Force constants for the linear CNO subsection of the molecule are strongly interrelated. The CN stretching force constant is somewhat lower than in acetonitrile, while the NO stretching force constant is relatively high, and a large interaction constant exists between these two modes of vibration. The values found for these constants in millidynes per angstrom unit are $F_{CN} = 17.526$, $F_{NO} = 9.358$, and $F_{CN,NO} = 0.90$. Similar results are found with respect to the linear bending motions associated with this subgroup. The force constants for these motions are $F_{CCN} = 0.397$ mdyn A, $F_{CNO} = 0.732$ mdyn A, and $F_{CCN,CNO} = 0.25$ mdyn. These results indicate that the CNO subsection of the molecule is best considered as a strongly interacting unit. The fact that the CN stretching force constant is lowered, but the absorption frequency raised (with respect to acetonitrile), may be accounted for by this strong interaction.

Studies of adducts of acetonitrile have shown that the CN stretching frequency increases upon adduct formation at the nitrogen atom.[2,3] Two postulates have been advanced to explain this frequency increase. The first of these is that the frequency increase is due to kinematic coupling between the CN and N-atom bonds in the adducts.[3] The second is based on electron redistribution, or hybridization changes, within the acetonitrile portion of the complex which results in a higher CN stretching force constant in the combination than in acetonitrile.[2] The frequency increase would thus be reflected by a force constant increase. Force constant calculations based on the observed infrared spectral frequencies for acetonitrile N-oxide should provide useful information concerning which of these postulates is more important.

The results of this study for acetonitrile N-oxide indicate that kinematic coupling between the CN and NO bonds in the molecule rather than an increase in the CN stretching force constant accounts for the observed increase in the CN stretching frequency. In acetonitrile adducts it has been shown that the CN stretching force constant increases.[2] An explanation for the difference in the two cases may be based on electron redistribution within the CN-atom portion of the molecule or adduct.

Experimental Section

Preparation of Acetonitrile N-Oxide. Acetonitrile N-oxide was prepared by the dehydrohalogenation of α-chloroacetaldoxime using triethylamine at $-40°$, according to the method described by Grundmann.[4] Small samples of the N-oxide were purified by sublimation under reduced pressure at approximately $-10°$ immediately prior to recording of spectra.

Acetonitrile N-oxide is unstable at room temperature, undergoing dimerization to form 3,4-dimethyl-1,2,5-oxadiazole 2-oxide (3,4-dimethylfuroxan). Decomposition is also evident. However, the N-oxide was found to be stable at Dry Ice temperature at which temperature the material was stored prior to use. The dimerization reaction begins quickly when samples are dissolved in a solvent or are allowed to become warm, necessitating scanning spectra as soon as possible. In order to identify absorption bands due to 3,4-dimethylfuroxan, and to eliminate these bands from consideration in the spectrum of acetonitrile N-oxide, the spectrum of 3,4-dimethylfuroxan was obtained from samples which were prepared independently, using the method of Scholl.[5]

Infrared Spectra. Spectra of acetonitrile N-oxide were obtained in solutions of CCl_4, CS_2, and cyclohexane. The spectra were recorded by means of Perkin-Elmer spectrophotometers, Models 137G, 21, and 621, and the Beckman IR5A CsBr spectrophotometer.

Results and Calculations

Calculations of vibrational frequencies were performed using the Wilson FG matrix method[6] and a set of symmetry coordinates corresponding to those used by Duncan[7] for acetonitrile and methylacetylene. *G* matrix elements were computed using the formulas given by Wilson[6] and later checked by Schachtschneider's program.[8] The molecular parameters for

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[1] Abstracted in part from the Ph.D. thesis of W. G. Isner, West Virginia University, 1967.

[2] K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966).

[3] T. L. Brown and M. Kubota, *ibid.*, **83**, 4175 (1961).

[4] C. Grundmann, "Methoden der Organischen Chemie," (Houben-Weyl, Ed., Band X/3, Georg Thieme Verlag, Stuttgart, 1965, p 849.

[5] R. Scholl, *Ber.*, **23**, 3490 (1890).

[6] E. B. Wilson Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[7] J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964).

[8] J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. V. Fortran IV Programs for Setting-up the Vibrational Secular Equations," Shell Development Co., Emeryville, Calif., 1966.

acetonitrile N-oxide were assigned reasonable values since no determination of molecular structure for the molecule has been made. The C–H, C–C, and C–N bond distances were assumed equal to the corresponding distances in acetonitrile (1.11, 1.46, and 1.16 A, respectively[9]), while the N–O distance was assigned a value of 1.25 A.[10] The angles at the methyl carbon atom were assumed to be tetrahedral.

The calculated *G* matrix, together with the observed vibrational frequencies and a trial set of symmetry force constants, were used as input to a force constant refinement program,[11] and the principal force constants were adjusted until the calculated vibrational frequencies agreed with the observed vibrational frequencies. Interaction force constants were held fixed at values approximately equal to the values used by Duncan[7] for similar molecules.

The observed vibrational frequencies for acetonitrile N-oxide, together with assignments to approximate modes of vibration based on C_{3v} symmetry, are given in Table I. The frequencies associated with the methyl group appear to be normal. The CC stretching vibration has been assigned at 778 cm^{-1} which is lower than normal. The CN stretching mode is observed at 2315 cm^{-1}, significantly higher than the corresponding absorption in acetonitrile (2266 cm^{-1}). The NO stretching frequency is assigned to an intense absorption band at 1319 cm^{-1} and is in the range reported for other nitrile N-oxides.[12] The CNO and CCN linear bending modes are assigned at 478 and 297 cm^{-1}, respectively.

Table I. Vibrational Frequencies and Assignments for Acetonitrile N-Oxide

Frequency, cm^{-1}	Assignment	Symmetry type
2967	CH stretch (asymmetric)	E
2924	CH stretch (symmetric)	A_1
2315	CN stretch	A_1
1441	CH_3 deformation (asymmetric)	E
1381	CH_3 deformation (symmetric)	A_1
1319	NO stretch	A_1
1177	CH_3 rock	E
778	CC stretch	A_1
478	CNO linear bend	E
297	CCN linear bend	E

Table II. Symmetry Force Constants (A_1 Species) for Acetonitrile N-Oxide, Acetonitrile, and Acetonitrile–Boron Trifluoride Adduct

Force constant[a]	CH_3-CNO	CH_3-CN	$CH_3CN \cdot BF_3$	
		Hybrid Orbital Force Field		
F_{CC}	5.043	5.156	5.371	4.779
$F_{CC,CN}$	0.30	0.30	0.30	0.30
$F_{CC,NO}$ or $F_{CC,NB}$	0.20	. . .	0.10	0.10
F_{CC,CH_3}def	−0.37	−0.37	−0.37	−0.37
F_{CN}	17.526	18.132	19.637	19.480
$F_{CN,NO}$ or $F_{CN,NB}$	0.90	. . .	0.50	0.50
F_{NO} or F_{NB}	9.358	. . .	2.027[b]	4.000[c]
F_{NO,CH_3} (or F_{NB,CH_3}) def	0.03	. . .	0.03	0.03
F_{CH}	4.936	5.038	4.972	4.974
F_{CH,CH_3} def	0.07	0.07	0.07	0.07
F_{CH_3} def	0.599	0.589	0.580	0.585
		Modified Valence Force Field		
F_{CC}	5.864	5.289	5.299	4.681
F_{CC,CH_3} def	−0.37	−0.37	−0.37	−0.37
F_{CN}	16.113	17.689	18.908	18.753
F_{NO} or F_{NB}	8.992	. . .	2.027[b]	4.000[c]
F_{CH}	4.918	5.022	4.957	4.959
F_{CH_3} def	0.577	0.589	0.582	0.587

[a] Stretching force constants in mdyn/A, bending force constants in mdyn A, and stretch–bend interactions in mdyn. [b] Force constant constrained at this value, corresponding to the treatment of Purcell and Drago.[2] [c] Force constant constrained at this value, which is considered to be an approximate upper limit for an NB stretching force constant (see ref 2).

Table III. Symmetry Force Constants (E Species) for Acetonitrile N-Oxide and Acetonitrile[a]

Force constant	CH_3CNO	CH_3CN
F_{CH}	4.739	4.875
F_{CH,CH_3} def	−0.13	−0.13
F_{CH,CH_3} rock	0.13	0.13
F_{CH_3} def	0.553	0.572
F_{CH_3} def, CH_3 rock	−0.05	−0.05
F_{CH_3} rock	0.889	0.684
F_{CCN}	0.397	0.265
$F_{CCN,CNO}$	0.25	. . .
F_{CNO}	0.632	. . .

[a] For hybrid orbital force field. See Table II, footnote *a* for units.

In order to compare the force constants calculated by the hybrid orbital force field for acetonitrile N-oxide with those for acetonitrile and an adduct of acetonitrile, calculations were also performed for acetonitrile and the boron trifluoride adduct of acetonitrile (A_1 symmetry species). Likewise, calculations were performed for acetonitrile N-oxide, acetonitrile, and the acetonitrile–boron trifluoride adduct using a modified valence force field corresponding to that used by Purcell and Drago.[2] The results of the calculations are reported in Tables II and III.

The interaction constants presented for $F_{CN,NO}$ (A_1) and $F_{CCN,CNO}$ (E) are the smallest values obtained that gave rapid convergence and a well-conditioned set in the force constant refinement program.[11]

Discussion

It may be seen from Tables II and III that there are no significant differences between force constants related to the methyl group for acetonitrile N-oxide and for acetonitrile when the hybrid orbital force field treatment is used. This correlates directly with the fact that the methyl group vibrational frequencies are essentially normal in the observed spectrum of acetonitrile N-oxide. The CC stretching force constant, F_{CC}, also compares quite closely with that in acetonitrile. This is remarkable since the absorption frequencies for this motion are quite different, being 918 cm^{-1} in acetonitrile and 778 cm^{-1} in acetonitrile N-oxide. This agreement of force constants in spite of

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[9] "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publication No. 11, The Chemical Society, London, 1958.

[10] Symmetry force constants were also calculated using N–O distances of 1.36 A (the value in trimethylamine N-oxide) and 1.19 A (N_2O). These sets of force constants were not significantly different from those calculated using an N–O distance of 1.25 A.

[11] W. T. Thompson and C. S. Shoup, University of Tennessee; modified by H. S. Kimmel, Newark College of Engineering, Newark, N. J.

[12] (a) R. H. Wiley and B. Wakefield, *J. Org. Chem.*, **25**, 546 (1960); (b) S. Califano, R. Moccia, R. Scarpatti, and G. Speroni, *J. Chem. Phys.*, **26**, 1777 (1957).

the difference in absorption frequencies reflects the fact that there is a high degree of interaction between this bond and the CNO portion of the acetonitrile N-oxide molecule.

The most significant difference between the force constants for acetonitrile and acetonitrile N-oxide is in the CN stretching force constants, F_{CN}. In acetonitrile N-oxide the CN stretching frequency is observed at 2315 cm^{-1}. In acetonitrile the frequency occurs at 2266 cm^{-1}. However, by using the same type of treatment for both molecules (hybrid orbital force field), F_{CN} is calculated to be lower for acetonitrile N-oxide than for acetonitrile. The frequency increase must therefore be due to coupling of the CN and NO stretching modes.

Another factor which should be considered in discussing the force constant relationships in acetonitrile, N-oxide is the exceptionally high value for the NO stretching force constant, F_{NO}. The value of this force constant, 9.358 mdyn/A indicates that the N–O bond in acetonitrile N-oxide has considerable double bond character.[13] In addition, the interaction constant, $F_{CN,NO}$ was found to have a relatively high value, indicating a high degree of interaction between the CN and NO stretching modes.

Essentially the same comments may be made concerning the vibrations of E symmetry in the CNO portion of the acetonitrile N-oxide molecule. The two linear bending modes have relatively high force constants, and a large interaction force constant for these two modes results.

The hybrid orbital force field calculations thus indicate that the vibrational modes and force constants for the CNO portion of the acetonitrile N-oxide molecule are strongly interrelated, *i.e.*, that no purely independent frequency exists in this portion of the molecule.

The modified valence force field calculations and the hybrid orbital force field calculations for $CH_3CN \cdot BF_3$ illustrate the differences between the adducts of acetonitrile and acetonitrile N-oxide. In both cases, the C–N stretching frequency is increased over that in acetonitrile, yet for $CH_3CN \cdot BF_3$, F_{CN} is higher than in acetonitrile and, in acetonitrile N-oxide, F_{CN} is lower. As has been noted for acetonitrile N-oxide, this frequency increase can be ascribed to kinematic coupling of the CN and NO stretching motions. For $CH_3CN \cdot BF_3$, on the other hand, the frequency increase is apparently due to an increase in F_{CN}. This increase occurs for both the hybrid orbital force field calculations in which the CN stretching–NB stretching interaction is taken into account ($F_{CN,NB} = 0.50$), and for the modified valence force field calculations in which no explicit allowance for such coupling is made. It is interesting to note that for $CH_3CN \cdot BF_3$ raising the N–B stretching force constant from 2.027 to 4.000 (see Table II) results in a slight decrease in F_{CN} (and in F_{CC}), indicating that perhaps interaction of the CN stretching and N-atom stretching modes is dependent on the strength of the N-atom bond.

The contrast in force constants for the C–N bond between acetonitrile N-oxide and the adducts of acetonitrile may be explained in terms of the electronic interactions which are possible in the two cases. For acetonitrile N-oxide, there may be assumed an increase in electron density in the N–O bond caused by the oxygen atom. This can result in a repulsion of the CN π electrons, thereby effectively lowering the electron density between the carbon and nitrogen atoms. This concept has been suggested by Grundmann[14] in a representation of resonance hybrid forms for nitrile N-oxides. The net result, in terms of force constants, is a decreased CN force constant (compared to acetonitrile) and a relatively high NO force constant. For the boron trifluoride adduct of acetonitrile, on the other hand, no such increase in electron density is possible, and thus the electron density between carbon and nitrogen is greater than in acetonitrile, resulting in a higher force constant for this bond. Extending this qualitative picture to acetonitrile, one might consider that the molecule represents an intermediate case in which the nitrogen lone-pair electrons repel the CN electrons to a slight extent, thereby lessening the electron density between the carbon and nitrogen atoms (compared to the boron trifluoride adduct) and resulting in a decrease in force constant.

We are initiating molecular orbital calculations in order to obtain more information regarding the explanations offered above for the differences observed for acetonitrile, its adducts, and acetonitrile N-oxide.

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(13) In nitrous acid the N—O force constant has a value of 3.15 mdyn/A, while the N=O force constant has a value of 11.95 mdyn/A: A. Palm, *J. Chem. Phys.*, **26**, 855 (1957).

(14) C. Grundmann, *Fortschr. Chem. Forsch.*, **7**, 62 (1966).