promise in this regard is the semiempirical SCF-MO method developed by Dewar and Klopman.[22] Use of these authors' eigenvector and eigenvalue data for CH_4 yields a value of +80.1 cps in this molecule. This compares with the extended Hückel value of +58.0 cps.

The calculations with PH_3 and PH_4^+ indicate that the ^{31}P–^{1}H coupling constant increases on going from a phosphine to a phosphonium cation. If the ^{31}P–^{1}H coupling constant of PH_4^+ is low by the same factor as that of PH_3 then J_{PH} of the phosphonium cation should be 562 cps (according to the extended Hückel with CNDO calculations), which is in fair agreement with the experimental value of 515 cps for the trimethylphosphonium cation.[23] The increase of J_{PH} on quaternization suggests the possibility of a linear relationship of this coupling constant with the s character of the bonding orbitals. However, it has been shown previously[24] that no such simple correlation exists.

Very recently it has been demonstrated[25] that the ^{13}C–^{13}C coupling constant is positive. By contrast the ^{31}P–^{31}P coupling constant is negative (the available data are shown in Table V). It may be that homonuclear directly bonded coupling constants of the third row are all negative. For this reason it would be interesting to know the sign of the ^{29}Si–^{29}Si coupling constant. The hybridizational and inductive effects on the ^{31}P–^{31}P coupling constant are not yet clear. The only obvious trend in the data in Table V is that the magnitude of J_{PP} increases when phosphorus is oxidized.

Acknowledgments. The authors are grateful to the Robert A. Welch Foundation for financial support and to Professor M. J. S. Dewar for helpful discussions. One of us (W. D. W.) is also grateful to Union Carbide for a predoctoral fellowship. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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Vibrational Spectra and Rotational Isomerism in Acrylyl Fluoride

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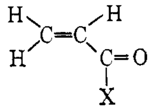
Abstract: A temperature-dependence study of the infrared spectrum of acrylyl fluoride has been carried out to obtain information on the rotational isomerism previously reported for this molecule. This study shows that, if a rotational equilibrium does exist, there is very little difference between the spectra of the two forms and the energy difference between the two forms is very small. The complete infrared and Raman spectra and their assignment on the basis of C_s symmetry are also reported. The torsional frequency about the C–C single bond was observed at 115 cm^{-1}, giving a barrier to internal rotation (V^*) of 18.6 kcal/mole.

There have been a number of recent papers concerning rotational isomerism[1,2] and torsional frequencies[3,4] in butadiene- and acrolein-type molecules. Of particular interest have been the acrylyl halides



In the case of the flouride, Koster[1] has shown by nmr methods that the molecule exists as an equilibrium mixture of an *s-trans* and an *s-cis* (or skew) form with an energy difference of 800 ± 250 cal/mole. Infrared studies on the chloride and bromide by Katon and Feairheller[2] have yielded similar results. These workers found that both acrylyl chloride and bromide exist in two forms and that the energy difference for the chloride was about 600 cal/mole.

Our interest in acrylyl fluoride was twofold. One difficulty in the calculation of potential barriers about the C–C single bond in conjugated molecules has been the lack of sufficient data to evaluate the relative magnitude of the various terms in the potential function.[4] This problem can be solved for a molecule which exists as an equilibrium mixture of two forms if the torsional frequency for each form and the energy difference between the two forms can be obtained. The acrylyl fluoride molecule appeared to be a promising case for obtaining these data. Secondly, we have recently described an improved method for the calculation of equilibrium constants from infrared data[5] and were interested in testing the method on additional molecules.

In this paper we are reporting on the results of an infrared investigation of the rotational equilibrium in acrylyl fluoride. Also included are the complete infrared and Raman spectra, an assignment of the fundamental vibrational frequencies, and the calculation of the barrier to internal rotation about the C–C single bond.

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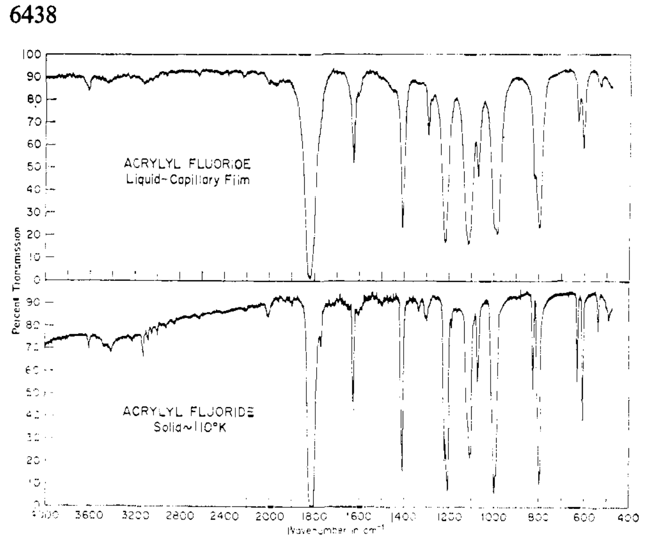


Figure 1. Infrared spectra of acrylyl fluoride as a liquid at +28° and as a solid at ~110°K.

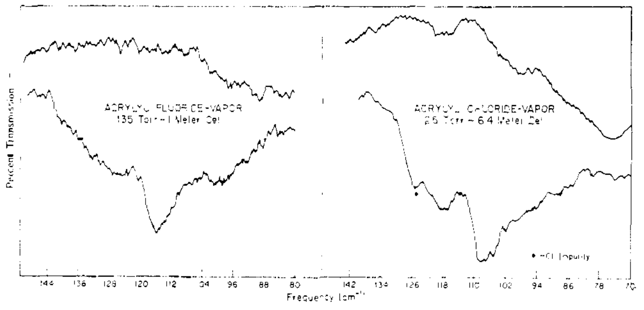


Figure 2. Torsional bands of acrylyl fluoride and acrylyl chloride. The weak HCl bands in the spectrum of the chloride are due to hydrolysis of the sample in the cell.

Experimental Section

The initial sample of acrylyl fluoride was obtained from Dr. D. F. Koster and was the same material used for his nmr studies.[1] Subsequent samples were prepared by the reaction of acrylyl chloride with SbF_3 according to the method of Brügel.[6] Both samples gave identical infrared spectra and boiling points (34.5° at 760 mm).

Infrared spectra were obtained on Beckman IR-9 (4000–400 cm^{-1}) and Beckman IR-11 (600–33 cm^{-1}) spectrophotometers. Liquid and gas spectra in the 4000–400-cm^{-1} region were obtained using conventional cells equipped with KBr or CsI windows. For the far-infrared region, polyethylene windows were used and vapor spectra were obtained with a Beckman multiple path cell at path lengths up to 8.2 m. Solid spectra were obtained by spraying the vapor on to a cold window in a dewar cell and annealing.

Variable-temperature infrared experiments were carried out with an RIIC variable-temperature cell (VTL-1). The temperature was monitored with a copper–constantan thermocouple and controlled to within ±2°. For the variable-temperature work, it was necessary to employ a solvent because acrylyl fluoride is very volatile, and it was not possible to hold the pure liquid at the small path lengths required to observe the bands of interest.

The Raman spectrum of liquid acrylyl fluoride was obtained using a Cary Model 81 Raman spectrometer with Hg 4358-A excitation. The sample decomposed or polymerized after about 0.5 hr in the arc, and repeated refilling of the sample tube was necessary in order to obtain all the measurements. Polarization measurements were made according to the method of Crawford and Horwitz.[7] The Raman spectrum of the liquid was also obtained at temperatures down to −100° using the dewar cell arrangement described by Miller and Matsubara.[8]

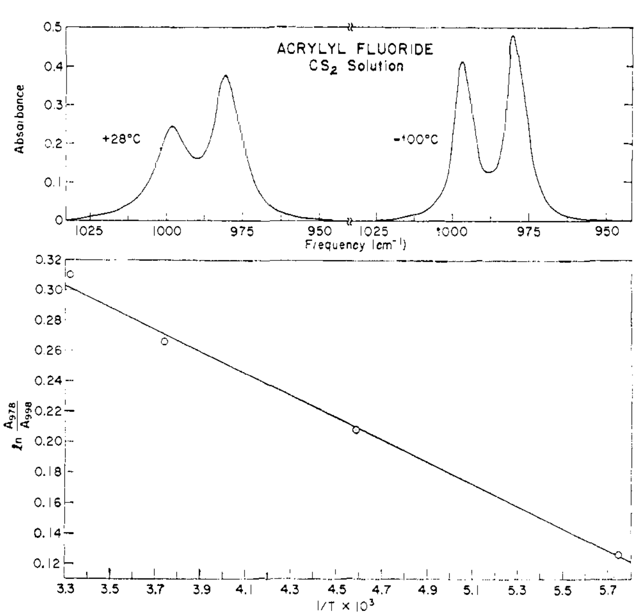


Figure 3. Top: Effect of temperature on the 978–998-cm^{-1} bands of acrylyl fluoride in CS_2 solution. Bottom: Plot of ln (A_{978}/A_{998}) *vs.* $1/T$ for acrylyl fluoride in CS_2 solution (slope = −75.5, ΔH = +150 cal/mole).

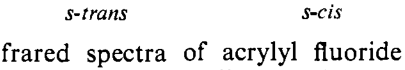
Results

The infrared frequencies for gaseous, liquid, and solid acrylyl fluoride and the Raman values for the liquid are given in Table I. The infrared frequencies for the liquid should be accurate to ±1 cm^{-1} throughout; values for the gas and solid and also the Raman data may be somewhat less accurate. The infrared spectra of the solid and liquid are compared in Figure 1, and the vapor band attributed to the torsion is shown in Figure 2.

Discussion

Rotational Isomerism. Katon and Feairheller[2] have shown that for acrylyl chloride and bromide there is significant simplification in their infrared spectra on going from the liquid to the low-temperature solid. These changes are particularly evident in the C–Cl and C–Br stretching regions and are explained by the presence of an equilibrium mixture of two forms in the liquid which revert to one form in the crystal.

Koster's nmr data indicate a similar occurrence for acrylyl fluoride and give ΔH = 800 cal/mole for the equilibrium between the *s-trans* and *s-cis* forms with the *s-trans* form being more stable at low temperature.[1]



Our infrared spectra of acrylyl fluoride as a gas, liquid, and solid are very similar and show no simplification on going from the liquid at room temperature to the crystal at liquid nitrogen temperature. Furthermore the Raman spectra of the liquid at +35 and −100° are nearly identical although these data could be misleading because of the low intensity of many of the lines and the wide slits required for the low-temperature measurements. The only apparent change in the

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Table I. Infrared and Raman Spectra of Acrylyl Fluoride

	Infrared, cm^{-1}		Raman		
Gas	Solid (~100°K)	Liquid	liquid	Assignment C_s symmetry[a]	
<60 v, br	~82 w–m	<100 s, vbr	Lattice or dipole–dipole absorption		
101 115 126 vw (pqr ?)		(120)		ν_{18} (torsion)	a''
~195 vw, br	182 vw			?	
269 277 286 w (pqr)	287 vw	285 w	287 12	ν_{13}	a'
395 vvw	393 vvw			115 (gas) + 277 (gas) = 392	A''
	452 vvw			?	
479 485 495 w (pqr)	489 vw	488 w	486 6	ν_{17}	a''
518 525 527 534 vw		522 w		2 × 120 + 285 = 525	A'
	538 w	535 w	535 6, pol?	ν_{12}	a'
608 619 636 m	606 m	606 m	608 4	ν_{16}	a''
	629 w–m	629 m	632 3, pol ?	ν_{11}	a'
800 803 s	800 s	800 s	810 826 16, pol	ν_{15}	a'
819 s	823 m	822 sh		285 + 535 = 820	a'
978 985 997 1010 s	990 sh	986 s		ν_{14} (*cis* isomer)	a''
			992 4, br		
	1000 vs	997 m, sh		ν_{14} (*trans* isomer)	a''
	1072 m	1074 m	~1078 ~1112 2, vbr	ν_{10}	a'
1117 1125 1133 vs (pqr)	1109 s	1114 s		ν_9	a'
1215 1232 s	1207 1222 s	1219 s	1220 4	ν_8	a'
1290 1297 1306 m (pqr)	1300 1308 w	1295 w	1297 25, pol	ν_7	a'
	1334 vw	1339 vw		120 + 1219 = 1339 535 + 800 = 1335	A'' A''
1403 1408 1411 1420 s	1409 s	1410 s	1411 35, pol	ν_6	a'
1462 w				?	
1626 1643 w	1610 vw	1610 vvw		535 + 1074 = 1609	A'
	1625 m	1628 m	1631 75, pol	ν_5	a'
	1770 w			538 + 1222 = 1760	A'
1839 1850 vs	1820 vvs	1819 vs	1818 100, pol	ν_4	a'
1950 w		1973 vw		2 × 986 = 1972	A'
2010 vw	2008 w	2005 vw		800 + 1219 = 2019	A''
3005 3015 vvw	3000 vvw		3004 20, pol	ν_3	a'
3050 3057 vw	3050 vw	3048 vw	3051 50, pol	ν_2	a'
	3090 vw	3093 vw	3095 10, pol	ν_1	a'
3115 3133 vw	3125 w	3125 w	3124 25	3004 + 120 = 3124	A''
	3225 vvw	3229 vw		1819 + 1410 = 3229	A'
3630 vw	3615 vw	3619 w		2 × 1819 = 3638	A'

[a] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. The value of 120 cm^{-1} for the torsion in the liquid is derived from combination tones.

infrared spectrum on going from liquid to solid involves the band near 1000 cm^{-1} as can be seen in Figure 1. In the liquid there are two badly overlapping bands at 986 and 997 cm^{-1}, in the solid only one band at 999 cm^{-1} with a shoulder near 990 cm^{-1}. In CS_2 solution the two bands become more separated as shown in Figure 3.

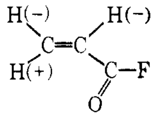
The obvious conclusion to be drawn from these data is that the infrared spectrum shows only very meager evidence for acrylyl fluoride existing as an equilibrium mixture of rotational isomers. This conclusion is, however, contradictory to the nmr results and implies two possibilities.

(1) The nmr results, which give evidence for an equilibrium mixture of two forms, are incorrect or apply only to acrylyl fluoride in $CFCl_3$ solution, and liquid acrylyl fluoride, unlike the chloro and bromo compounds, exists in only one form. The fluoride

would then be similar to acrolein where no evidence for a second isomer could be found.[9]

(2) The infrared and Raman spectra of the *s-trans* and *s-cis* (or skew) isomers of acrylyl fluoride are virtually identical with the only observable difference being the changes near 1000 cm^{-1} as mentioned above. This is very different from the case of the chloride and bromide where many of the fundamental frequencies were found to differ by as much as 25 cm^{-1} in the two forms. One rationalization of these data could be that oxygen and fluorine of the -C(=O)F rotor have similar masses and electronegativities and interchanging them by internal rotation has a much smaller effect on the spectrum than interchanging the oxygen and chlorine in the -C(=O)Cl rotor. In addition there is some precedence for rotational isomers having nearly identical infrared spectra. Hirschmann, Kniseley, and Fassel[10] found that the spectra of some alkyl thiocyanates showed only one band that was not common to both isomers.

The 986–997-cm^{-1} band in acrylyl fluoride is most likely due to a vibration of the form[11]



but the reason for this mode having a larger frequency difference in the two forms than any of the other fundamentals is not immediately obvious.

If acrylyl fluoride does exist as an equilibrium mixture of two forms, the two bands near 1000 cm^{-1} should show temperature-dependent changes in their relative intensities. A very careful study of these bands in CS$_2$ solution over the range +28 to −100° gave some indication that the higher frequency component increased in intensity relative to the lower as shown in Figure 3. Because of serious overlap of the bands, accurate integrated intensity measurements were exceedingly difficult. The "minimum" method described by Baker and Yeaman[12] was used to separate the areas of the overlapping bands, and the areas were measured with a hand planimeter. The measured areas and their ratios as a function of temperature are given in Table II and the standard ln (A_{981}/A_{996}) *vs.* $1/T$ plot is shown in Figure 3.

Table II. Integrated Intensities As a Function of Temperature for the 998- and 978-cm^{-1} Bands of Acrylyl Fluoride[a]

Temp, °K	$A_{998\text{cm}^{-1}}$	$A_{978\text{cm}^{-1}}$	$A_{978\text{cm}^{-1}}/A_{998\text{cm}^{-1}}$
301	195	266	1.36
268	200	261	1.305
218	203	250	1.23
174	212	241	1.135

[a] Frequencies and intensities are for a dilute solution in CS$_2$. The *A* values are arbitrary planimeter units.

The data reasonably meet the requirements which we have recently described for the measurement of conformational equilibria by infrared techniques[5] and give a ΔH of $+150 \pm 100$ cal/mole and an equilibrium constant of approximately 1 at room temperature for the *trans* ⇄ *cis* isomerism. Because Koster has shown that the *trans* form is more stable at low temperatures, we would assign the 998-cm^{-1} band to the *trans* form and the 978-cm^{-1} band to the *cis*. This assignment also agrees with the changes on going from liquid to solid where the higher frequency component persisted in the solid at low temperature.

Our ΔH value of 150 cal/mole for acrylyl fluoride in CS$_2$ solution does not agree with the nmr value of 800 cal/mole for a CFCl$_3$ solution.[1] One reason could be that the measurements were made using quite different solvents, and the solvent has a large effect on the equilibrium. Unfortunately it was not possible to carry out the infrared study in CFCl$_3$ because of very strong solvent absorption at 1000 cm^{-1}. However the effect of solvent polarity was tested by measuring the spectrum of acrylyl fluoride in the 1000-cm^{-1} region in dimethylformamide. In this very polar solvent only one, somewhat broad, band peaking at 998 cm^{-1} was observed, indicating that the equilibrium is a function of solvent polarity and that the *trans* form is more stable in polar solvents. It would also appear that the equilibrium constant for the neat liquid is about the same as that found for the CS$_2$ solution because the relative intensities of the two bands near 1000 cm^{-1} are roughly the same in the liquid and CS$_2$ solutions.

It must be concluded that this study does not unequivocally resolve the problem of rotational isomerism in acrylyl fluoride. The very small differences between the infrared spectrum of the liquid and the low-temperature solid would certainly not lead one to suspect the presence of an equilibrium mixture of isomers. However, the fact that the one observable temperature-dependent change does fulfill the requirements for a conformational equilibrium could indicate a rotational equilibrium, particularly because the nmr study of Koster has shown this to be the case. Therefore if acrylyl fluoride does exist as an equilibrium mixture of rotational isomers, the results of this study show (1) the energy difference between the two forms is very small in CS$_2$ solution, and probably also very small for the neat liquid; (2) the equilibrium constant is strongly influenced by the dielectric properties of the solvent, with more polar solvents favoring the *s-trans* form.

Vibrational Assignment. Acrylyl fluoride, either as the *cis* or *trans* isomer, possesses only a plane of symmetry and therefore falls into the C_s point group. This gives rise to 18 fundamental vibrational frequencies, all infrared and Raman active, and, although an unambiguous assignment is impossible, it is worthwhile to show that all features of the spectrum can be explained on the basis of only one isomeric form.

The assignment using Herzberg's conventions[13] is given in Tables I and III. Frequency values given in Table III are for the liquid, and the assignment was made by consideration of the assignment for acrolein[14] and characteristic group frequencies.[11,15]

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Table III. Vibrational Assignment for Acrylyl Fluoride. C_s Symmetry

Species	Activity[a]	Vibr no.	Approx description	Cm^{-1} (liq)
a′	R, pol, ir	1	CH stretch	3095
		2	CH stretch	3051
		3	CH stretch	3004
		4	C═O stretch	1819
		5	C═C stretch	1628
		6	CH_2 scissors	1410
		7	CH bend	1295
		8	C—C stretch	1220
		9	C—F stretch	1114
		10	CH_2 rock	1074
		11	C—F bend	632
		12	C—C═C bend	535
		13	C—C═O bend	285
a″	R, dp, ir	14	CH_2 twist	997[b] 986
		15	CH_2 wag	800
		16	CH wag	606
		17	CF wag	488
		18	Torsion	(120)[c]

[a] R = Raman; ir = infrared. [b] Attributed to *cis* and *trans* forms. [c] The 120-cm^{-1} torsion was derived from combination bands for the liquid. It was actually observed at 115 cm^{-1} in the gas.

The in-plane (a′) C—H, C═O, and C═C stretches and the in-plane modes of the vinylidene group are readily assigned on the basis of known group frequencies and the Raman polarization data. The high intensity of the infrared band at 1114 cm^{-1} makes it a reasonable choice for the C–F stretching vibration. This leaves 1220 cm^{-1} for the C–C stretching frequency, somewhat higher than the 1158-cm^{-1} value given for acrolein. The three remaining in-plane modes must be assigned to the polarized Raman lines at 632, 535, and 285 cm^{-1}, but, because these vibrations are probably mixed, the descriptions given in Table III must be regarded as only speculative. This accounts for all of the polarized Raman lines except the 800–822-cm^{-1} doublet which will be discussed below.

The assignment of the out-of-plane (a″) vibrations of the vinylidine group are straightforward except for the CH_2 wag (ν_{16}). This vibration usually falls near 910 cm^{-1} but should be lowered in acrylyl fluoride by the acid fluoride group. Thus the CH_2 wag is assigned at 800 cm^{-1}, and the apparent polarization of this line in the Raman spectrum is thought to result from the presence of an A′ combination band at 822 cm^{-1}. The assignment of 488 cm^{-1} as the a″ C–F wag places this mode somewhat lower than the analogous a′ vibration as would be expected.

This completes the assignment except for the torsion and accounts for all of the Raman lines except 3124 cm^{-1}. Because the 3124-cm^{-1} line is strongly depolarized, it must be an a′ + a″ combination. But since the highest a″ mode is at 986 cm^{-1}, there is no binary which can explain this band except for a low a″ frequency, the torsion, in combination with one of the C–H stretches. The combination 3004 (ν_3, a′) + 120 = 3124 cm^{-1} predicts the torsion at 120 cm^{-1} and agrees nicely with a band observed in the gas at 115 cm^{-1}. In addition a fundamental frequency near 120 cm^{-1} is useful in explaining other weak bands in the spectrum as shown in Table II.

The remaining features of the spectrum of the gas, liquid, and solid can be readily explained on the basis of only one isomeric form except for the 986–997-cm^{-1} doublet as discussed in the previous section.

Barrier to Internal Rotation. The potential function hindering internal rotation around the C–C single bond in conjugated molecules has been discussed in an earlier paper.[4] This potential function is of the form

$$V(\alpha) = \frac{V_1}{2}(1 - \cos \alpha) + \frac{V_2}{2}(1 - \cos 2\alpha) + \frac{V_3}{2}(1 - \cos 3\alpha)$$

(when V_4 and higher terms are neglected), and one major problem has been the lack of sufficient data to evaluate the V_1, V_2, and V_3 terms in the expression. As mentioned previously, this problem can be solved if the torsional frequency for each rotational isomer and the energy difference between the isomers can be obtained.

Since there is reasonably good evidence that acrylyl fluoride could exist with high concentrations of both rotamers, we looked very hard for the torsions for each form. Unfortunately it appears that there is only one torsional frequency, and, if there are two forms present, the torsions, like nearly all of the other vibrational frequencies, are the same for the two forms.

Acrylyl chloride is also of particular interest in this respect because Katon and Feairheller[2] have shown that it definitely exists in two forms, and, although unable to observe the torsion, they did find that several of the fundamentals had different frequencies in the two forms. Koster, however, has recently measured the far-infrared spectrum of gaseous acrylyl chloride and could find only one torsional frequency at 108 cm^{-1}.[16] This band and the 115-cm^{-1} band of the fluoride are shown in Figure 2. The shapes of these bands are very similar to the torsional bands of acrolein and butadiene.[4]

In the absence of two torsional frequencies we can only calculate a total barrier height, V^*, where V^* is defined as $V^* = V_1 + 4V_2 + 9V_3$. The 0 → 1 torsional transition is related to V^* by the expression

$$V^* = \bar{\nu}^2/F$$

where F, a reduced moment of inertia constant, is calculated from the geometry of the molecule. The F's for acrylyl fluoride and acrylyl chloride, calculated by computer from the method described by Pitzer,[17] are 2.0268 and 1.9606 cm^{-1}, respectively. Barrier heights (V^*) calculated from these values and the torsional frequencies are 6530 cm^{-1} (18.65 kcal/mole) for the fluoride and 5950 cm^{-1} (17.0 kcal/mole) for the chloride. These values are somewhat lower than the 21.2-kcal/mole barrier found for acrolein.[4]

Acknowledgment. We wish to thank Dr. David Koster for suggesting this problem to us and for the use of the low-frequency data on acrylyl chloride.

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We also wish to thank Dr. J. E. Katon for providing us with a copy of his manuscript prior to publication. This work was partially supported by the National Science Foundation, Grant GP-6112, the National Institutes of Health, Grant No. GM-11815, and Mellon Institute.

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

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Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506. *Received July 25, 1967*

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 $F_{\text{CN}} = 17.526$, $F_{\text{NO}} = 9.358$, and $F_{\text{CN,NO}} = 0.90$. Similar results are found with respect to the linear bending motions associated with this subgroup. The force constants for these motions are $F_{\text{CCN}} = 0.397$ mdyn A, $F_{\text{CNO}} = 0.732$ mdyn A, and $F_{\text{CCN,CNO}} = 0.25$ 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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