

Emission spectroscopy of the predissociative excited state dynamics of acrolein, acrylic acid, and acryloyl chloride at 199 nm

Michael F. Arendt, Paul W. Browning, and Laurie J. Butler

The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

(Received 17 May 1995; accepted 30 June 1995)

The emission spectroscopy of acrolein ($\text{C}_3\text{H}_4\text{O}$), acrylic acid ($\text{C}_2\text{H}_3\text{COOH}$), and acryloyl chloride ($\text{C}_2\text{H}_3\text{COCl}$) excited at 199 nm elucidates the dominant electronic character of the excited state reached by the optical transition at this wavelength. Progressions in the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching overtones and various combination bands suggest the antibonding orbital has mixed $\pi^*(\text{C}=\text{C})/\pi^*(\text{C}=\text{O})$ character. We interpret the results in conjunction with *ab initio* calculations at the configuration interaction singles level to identify the influence of resonance in the excited state of these conjugated molecules. The results on acrylic acid are of particular interest as excitation in this absorption band produces the HOCO intermediate of the $\text{OH}+\text{CO}\rightarrow\text{H}+\text{CO}_2$ reaction that is important in combustion. © 1995 American Institute of Physics.

I. INTRODUCTION

We undertook the study of the emission spectroscopy of acrylic acid excited at 199 nm to understand the dynamics in the Franck–Condon region of the predissociative excited state. This system is of particular interest because previous workers¹ had shown that photodissociation in the 185 nm absorption band generates the photoproduct HOCO, which is the intermediate of the $\text{OH}+\text{CO}\rightarrow\text{H}+\text{CO}_2$ reaction important^{2,3} in combustion processes. We followed our study of the emission spectrum of acrylic acid with studies of the related molecules acrolein and acryloyl chloride to aid in assigning and interpreting the emission spectra. The excitation wavelength of 199 nm was selected because it is well within the envelope of the absorption band for each of the three molecules, but shifted to the red of the absorption maxima. Previously, the excited state of acrylic acid accessed in this region was believed to be to a state with primary $\pi^*(\text{C}=\text{C})$ character. Our results, however, evidence a mixed $\pi^*(\text{C}=\text{C})/\pi^*(\text{C}=\text{O})$ character for the excited state of all three of these conjugated molecules.

Emission spectroscopy of dissociating molecules or resonance Raman scattering through a dissociative excited state is useful in spectroscopically probing the dynamics of molecules as they photodissociate. The time-dependent theory of resonance Raman spectroscopy was first introduced by Heller⁴ and experimentally by Imre and Kinsey⁵ in their study of the dissociation of methyl iodide (CH_3I). In the time domain, emission spectroscopy involves excitation of a molecular wave packet from the ground state to an excited potential energy surface via a resonant Franck–Condon electronic transition. The excited potential surface is usually dissociative in one or more bond coordinates. Due to the forces in the Franck–Condon region, the molecular wave packet will move along the dissociative potential energy surface, and as it does so, the wave packet will develop Franck–Condon overlap with higher vibrational states in the ground potential energy surface. In general, a small fraction of the molecules (1 in 10^5) will reemit to the ground state, while a majority of the molecules will dissociate. The photons that

are emitted give a spectrum which represents the dynamics of the molecule as it photodissociates.

In the molecules investigated in this paper, the excited state is predissociative rather than directly repulsive in a given bond-breaking coordinate. The early dynamics reflected in the emission spectrum, which could equally accurately be called a dispersed fluorescence spectrum, is then dominated by stretching of the molecular bonds in which the excited state equilibrium geometry is displaced from that of the ground state, not by bond fission dynamics. The spectra can thus elucidate the character of the excited state in the Franck–Condon region.

Of the three molecules under study in this paper, acrolein has received the most attention to date.^{6,7} It was Walsh⁶ who first identified the transition centered at 193.5 nm to be to a state of mixed $\pi^*(\text{C}=\text{C})/\pi^*(\text{C}=\text{O})$ character. The transition is also believed to have a contribution from an intramolecular charge-transfer⁷ band also centered around 193.5 nm. Previous electronic structure calculations of acrylic acid⁸ assigned the electronic absorption band peaking near 185 nm as a $\pi\rightarrow\pi^*$ transition centered on the vinyl group. The calculations were performed using the molecular geometries obtained from the electron diffraction studies of Ukaji *et al.*⁹ and the semiempirical quantum mechanical CNDO-CI complete neglect of differential overlap with configuration interaction method. The differing assignments of the absorption spectra motivated our emission spectroscopy experiments and *ab initio* calculations.

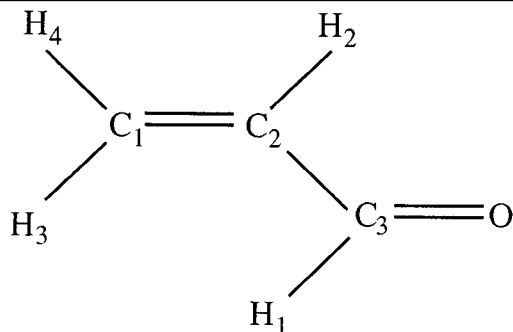
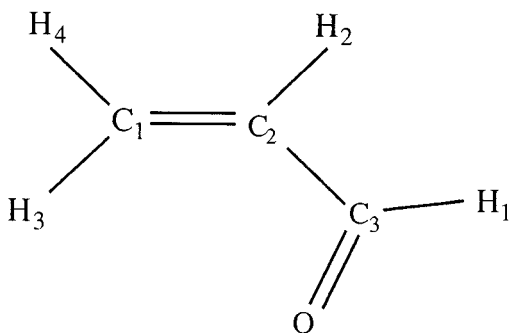
The emission spectra measured in the present study show that the excited state has mixed $\text{C}=\text{C}/\text{C}=\text{O}$ π antibonding character in all three molecules. We present supporting *ab initio* electronic structure calculations that in conjunction with the experimental results, determine the dominant electronic character of the excited state reached in the 199 nm absorption band of these molecules.

II. EXPERIMENTAL METHOD

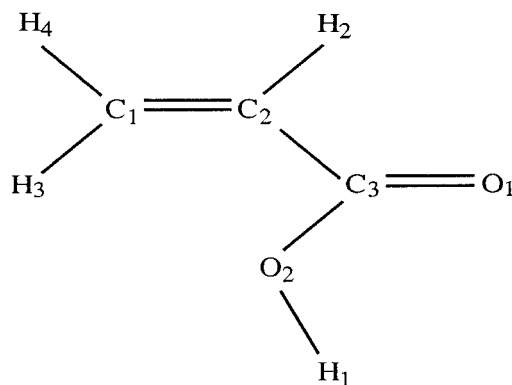
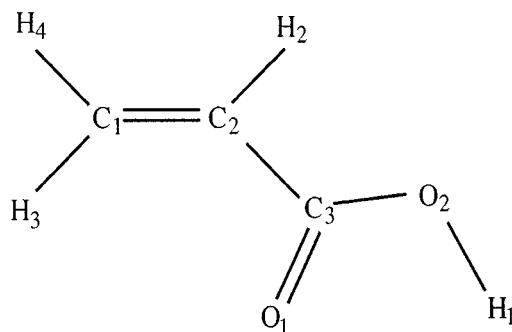
In order to obtain the excitation wavelength of 199 nm needed in this experiment, the doubled output of a Quantel YG 581-C Nd:YAG laser with a pulse duration of 20 ns and

TABLE I. Structural parameters for *s-trans* and *s-cis* acrolein obtained from microwave spectroscopy studies. All lengths are measured in units of angstroms (Å).

Structural parameter	Microwave spectroscopy	
	<i>s-trans</i>	<i>s-cis</i>
C ₁ =C ₂	1.345	1.345
C ₂ —C ₃	1.470	1.470
C ₃ —H ₁	1.108	1.108
C ₃ =O	1.219	1.219
C ₂ —H ₂	1.086	1.086
C ₁ —H ₃	1.086	1.086
C ₁ —H ₄	1.086	1.086
∠C ₁ —C ₂ —C ₃	119.8	119.8
∠C ₂ —C ₃ —H ₁	115.1	115.1
∠C ₂ —C ₃ —O	123.3	123.3
∠C ₁ —C ₂ —H ₂	120.0	120.0
∠H ₃ —C ₁ —C ₂	121.5	121.5
∠H ₄ —C ₁ —C ₂	117.3	117.3
C ₁ =C ₂ —C ₃ =O dihedral angle	180.0°	0.0°

*s-trans* Acrolein*s-cis* AcroleinTABLE II. Structural parameters for *s-trans* and *s-cis* acrylic acid obtained from microwave spectroscopy studies. All lengths are measured in units of angstroms (Å).

Structural parameter	Microwave spectroscopy	
	<i>s-trans</i>	<i>s-cis</i>
C ₁ =C ₂	1.345	1.345
C ₂ —C ₃	1.470	1.470
C ₃ —O ₁	1.343	1.343
C ₃ =O ₂	1.202	1.202
O ₁ —H ₁	0.972	0.972
C ₂ —H ₂	1.084	1.084
C ₁ —H ₃	1.086	1.086
C ₁ —H ₄	1.086	1.086
∠C ₁ —C ₂ —C ₃	119.5	119.5
∠C ₂ —C ₃ —O ₂	123.5	123.5
∠C ₃ —O ₁ —H ₁	106.3	106.3
∠O ₁ —C ₃ —O ₂	123.5	123.5
∠H ₂ —C ₂ —C ₃	117.3	117.3
∠H ₃ —C ₁ —C ₂	120.0	120.0
∠H ₄ —C ₁ —C ₂	120.0	120.0
C ₁ =C ₂ —C ₃ =O ₁ dihedral angle	180.0°	0.0°

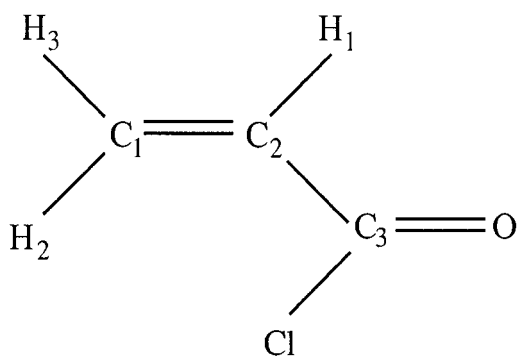
*s-trans* Acrylic acid*s-cis* Acrylic acid

pulse energy of 350 mJ/pulse is used to pump a Lambda Physik FL3002 dye laser at 20 Hz. The dye laser is tuned to 597 nm within the lasing range of Rhodamine 610 dye; an intracavity etalon reduces the bandwidth from approximately 0.2 to 0.05 cm⁻¹. Two stage amplification within the dye laser increases the overall output to 60 mJ/pulse. The output of the dye laser is then doubled in frequency via second-

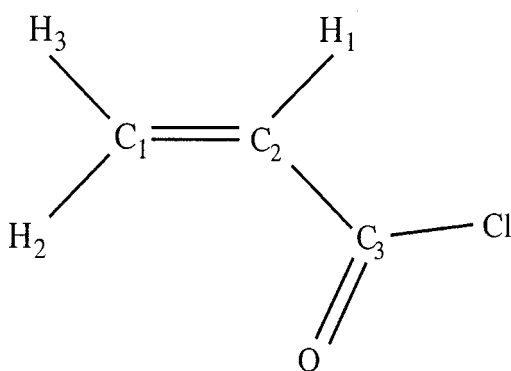
harmonic generation in a potassium-dihydrogen phosphate (KDP) crystal. The output of the dye laser is polarized perpendicular to the plane of the laser table, while the 298.5 nm doubled light has a polarization which is parallel to the plane of the table. Both the 597 and 298.5 nm beams are directed towards a dichroic beam splitter which will transmit the vis-

TABLE III. Structural parameters for *s-trans* and *s-cis* acryloyl chloride obtained from microwave spectroscopy and electron diffraction studies, respectively. All lengths are measured in units of angstroms (Å).

Structural parameter	Microwave spectroscopy <i>s-trans</i>	Electron diffraction <i>s-cis</i>
C ₁ =C ₂	1.345	1.339
C ₂ —C ₃	1.476	1.484
C ₃ —Cl	1.816	1.772
C ₃ =O	1.192	1.192
C ₁ —H ₁	1.086	1.100
C ₁ —H ₂	1.086	1.100
C ₂ —H ₃	1.084	1.100
∠C ₁ —C ₂ —C ₃	122.6	123.4
∠C ₂ —C ₃ —Cl	116.3	111.8
∠C ₂ —C ₃ =O	127.2	125.2
∠H ₁ —C ₁ —C ₂	121.5	121.5
∠H ₂ —C ₁ —C ₂	120.0	121.5
∠H ₃ —C ₂ —C ₁	117.4	121.5
C ₁ =C ₂ —C ₃ =O dihedral angle	180.0°	0.0°



s-trans Acryloyl chloride



s-cis Acryloyl chloride

ible (597 nm) light and reflect the ultraviolet (298.5 nm) light. The ultraviolet light is sent through a half-wave plate in order to rotate the polarization by 90 degrees and then spatially recombined with the visible light with another dichroic beam splitter and passed through the BBO crystal which generates the 199 nm output beam via sum frequency mixing¹⁰ the fundamental (598 nm) with the frequency

doubled ultraviolet (298.5 nm) light. The conversion efficiency for each nonlinear crystal is on the order of 10%, thus giving us 199 nm at approximately 350–400 μJ/pulse from the initial dye laser fundamental pulse energy of approximately 50–60 mJ/pulse.

The 199 nm frequency tripled output of the dye laser is first spatially separated from the residual visible and ultraviolet light by a Pellin–Broca prism and then passed through a stainless steel cell where it photodissociates the molecules in the sample gas. The emitted light is collected orthogonal to the direction of propagation of the excitation laser beam. The cell is kept at room temperature and helium is pumped into the cell in order to flush the sidearms of the cell. The total pressure in the cell is approximately 4.5 Torr, with 4 Torr of helium and 0.5 Torr of sample. The cell is continuously pumped in order to remove any excess photofragments, so as to reduce the chances of contamination of the spectrum from secondary reactions of the photofragments.

The emitted light is then recollimated, passed through a depolarizing wedge optic, and imaged onto the entrance slit (75 μm) of a Spectra-Pro 0.275 m spectrometer. The light is then dispersed by a 1200 grooves/mm Milton–Roy holographic grating onto an EG&G 1455 B-700 HQ Optical Multichannel Analyzer (OMA), which consists of a 18 mm photodiode array of 700 pixels, covering a 50-nm-wide emission spectrum. The resolution of the OMA is limited by the grating, path length, and intensifier resolution (3 pixels) to 75 cm^{−1}. The detector is cooled to a temperature of −30 °C and the intensifier is gated by an amplified transistor–transistor logic pulse that is synchronized to the laser with a set delay from the Nd:YAG Q switch. The OMA intensifier is “on” for only 200 ns around each laser pulse, so as to reduce the background noise from dark counts in the photodiode array. The OMA is connected to an IBM-compatible computer which collects and displays the data. Each scan is collected for 100 s at 20 Hz, or approximately 2000 laser shots per scan. The spectrum of acrolein was collected over 100 scans and is summed over 200 000 laser shots. The spectrum of acrylic acid consists of 200 scans and is summed over 400 000 laser shots. Similarly, the spectrum for acryloyl chloride consists of 100 scans and is summed over 200 000 laser shots.

Acrolein (97%), acrylic acid (99%), and acryloyl chloride (98%) were all obtained from Aldrich Chemical Company and were not distilled prior to use. The acrolein was stabilized with 0.1 wt % hydroquinone, the acrylic acid with 200 ppm hydroquinone monomethyl ether, and the acryloyl chloride with phenothiazine, so as to prevent polymerization. None of these additives have been shown to effect the observed spectra. Acrolein (C₃H₄O), acrylic acid (C₂H₃COOH), and acryloyl chloride (C₂H₃COCl) all share a similar C=C–C=O backbone. All three molecules exists as a mixture of two isomers, *s-cis* and *s-trans*. The *s-trans* conformer for acrolein has been found to be the more stable of the two by approximately 2.3 kcal/mol.¹¹ In the case of acrylic acid the *s-cis* conformer is more stable by approximately 360±100 cal/mol.¹² Similarly, acryloyl chloride can exist as *s-cis* and *s-trans* conformers, however, the *s-trans* conformer has been

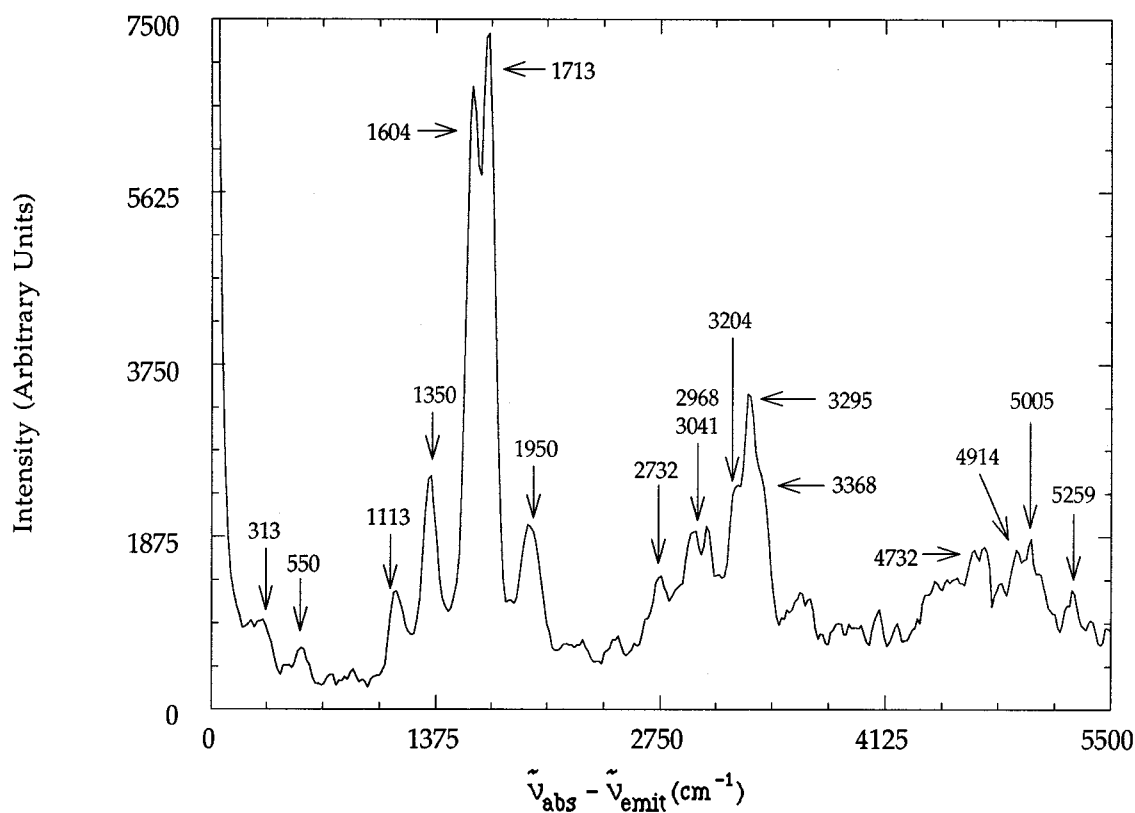


FIG. 1. Emission spectrum of acrolein taken at an excitation wavelength of 199 nm. Emission is seen corresponding to progressions in the C=C and C=O stretching overtones and various combination bands. Assignment of peaks is given in Table IV.

found to be more stable by approximately 600 cal/mol¹³ over the *s-cis* conformer.

III. COMPUTATIONAL METHOD

In order to better interpret the experimental results, *ab initio* calculations were performed on acrolein, acrylic acid, and acryloyl chloride using the GAUSSIAN 92 set of programs.¹⁴ These calculations are intended to help characterize the excited state to which these molecules are promoted at 199 nm. The configuration interaction with single excitations (CIS) used a 6-31G* basis set and a restricted Hartree-Fock (RHF) reference determinant. All calculations were performed on a Silicon Graphics 4D/280 mainframe with 128 MB and 6 processors (2×33 MHz and 4×25 MHz) under the IRIX:4.0.5 operating system.

The structural parameters used in the GAUSSIAN 92 calculations were obtained from previously performed microwave spectroscopy¹⁵⁻¹⁷ and electron diffraction studies.¹⁸ A complete listing of the experimental geometries for *s-cis* and *s-trans* acrolein can be found in Table I, for *s-cis* and *s-trans* acrylic acid in Table II, and a similar listing for *s-cis* and *s-trans* acryloyl chloride in Table III.

IV. RESULTS AND ANALYSIS

The emission spectrum of gaseous acrolein at 199 nanometers is shown in Fig. 1 with peaks assignments given in Table IV. The positions of the peaks in the emission spectrum are assigned according to the lines previously deter-

mined by Harris¹⁹ in his study of the Raman spectrum of gaseous acrolein. The major peaks in the emission spectrum can be assigned to progressions in both the C=C and C=O stretch, with a maximum of three quanta in each. There are also several lines corresponding to the CH₂ wag and twist

TABLE IV. Acrolein emission spectrum peak assignments.

Description	Accepted value ^a in cm ⁻¹	Experimental value ^b in cm ⁻¹
C=C skeletal bend	327	313
C=O skeletal bend	564	550
C-C stretch	1158	1113
C-H bend	1360	1350
C=C stretch	1625	1604
C=O stretch	1724	1713
2×CH ₂ twist, 2×CH ₂ wag	1918,1986	1950
C-H stretch	2800-3000	2732,2968,3041
2×C=C stretch	3248	3204
C=C stretch+C=O stretch	3349	3295
2×C=O stretch	3448	3368
3×C=C stretch	4875	4732
2×C=C stretch+C=O stretch	4974	4914
C=C stretch+2×C=O stretch	5073	5005
3×C=O stretch	5172	5259

^aFrom Ref. 19.

^bOur results given the maximum resolution of 75 cm⁻¹ with current monochromator.

TABLE V. Molecular orbitals in the 6-31G* basis making the largest contributions to the electronic transition in acrolein (C_3H_4O) as calculated by GAUSSIAN 92. The molecule is oriented in the XZ plane with the first vinylic carbon atom at the origin.

Atom/atomic orbital	Orbital coefficient ground state	Orbital coefficient excited state
<i>s-trans</i> acrolein (C_3H_4O)		
$C_1/2p_y$	0.344 12	0.325 13
$C_1/3p_y$	0.288 74	0.541 22
$C_2/2p_y$	0.350 49	-0.208 11
$C_2/3p_y$	0.286 34	-0.360 49
$C_3/2p_y$	-0.043 71	-0.274 91
$C_3/3p_y$	-0.040 16	-0.345 22
$O/2p_y$	-0.242 25	0.282 40
$O/3p_y$	-0.200 66	0.341 08
<i>s-cis</i> acrolein (C_3H_4O)		
$C_1/2p_y$	0.338 31	0.314 60
$C_1/3p_y$	0.264 50	0.547 73
$C_2/2p_y$	0.361 90	-0.189 17
$C_2/3p_y$	0.312 78	-0.346 09
$C_3/2p_y$	-0.037 92	-0.278 77
$C_3/3p_y$	-0.045 92	-0.363 16
$O/2p_y$	-0.244 96	0.266 32
$O/3p_y$	-0.198 10	0.340 00

motions. Also, an emission line to a level with one quantum of stretch in the C–C bond appears in the spectrum. The spectrum indicates that in the excited state the equilibrium bond length of both the C=C and C=O bonds differ from that of the ground state.

In order to better understand the nature of the optical transition at 199 nanometers, a series of *ab initio* calculations using the GAUSSIAN 92 set of programs were performed on both *cis* and *trans* acrolein. The results are given in Table V. In agreement with Walsh, the transition at 199 nanometers is shown by our calculations to be to a state consisting of a mixture of π^* antibonding character on both the C=C and C=O bonds. Pictures of the relevant molecular orbitals for the ground and excited state are given in Fig. 2.

The emission spectrum of gaseous acrylic acid at 199 nanometers is shown in Fig. 3 with peak assignments listed in Table VI. The peaks are assigned according to the Raman lines identified for this compound by Katon and Fairheller²⁰ in an earlier experiment involving liquid acrylic acid. It was believed that the excitation of this molecule at 199 nm was to a state which had primary π^* character in the C=C bond. This is partially confirmed by our emission spectrum which has peaks corresponding to a progression of up to four quanta in the C=C bond stretch. However, in addition to the C=C stretch, our emission spectrum shows additional peaks corresponding to a similar progression of up to four quanta in the C=O bond coordinate. Indeed the spectrum is very similar to that obtained for acrolein, when the excited state π^* orbital is an admixture of $\pi^*(C=C)/\pi^*(C=O)$ character. The spectrum thus suggest that excitation at 199 nm does not yield a pure $\pi \rightarrow \pi^*$ transition centered on the vinyl group as previously assigned, but that rather the π^* orbital is of mixed character.

In an attempt to further identify the character of the tran-

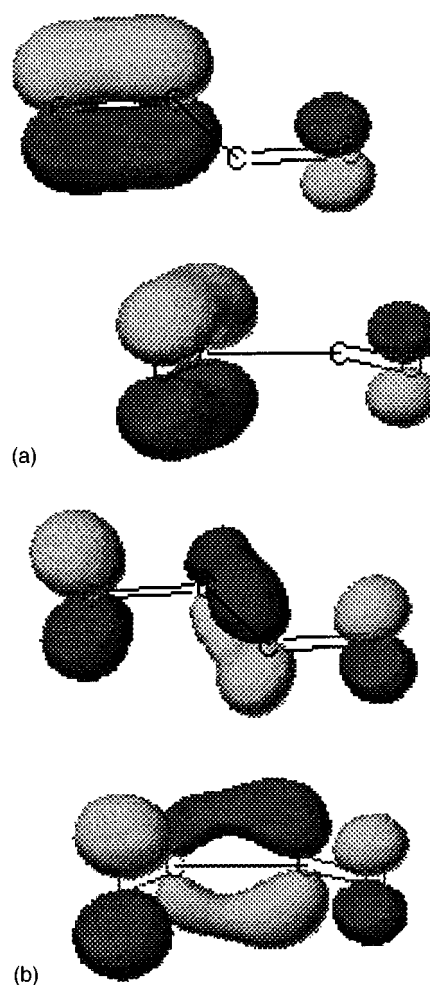


FIG. 2. (a) Ground state molecular orbitals for *s-trans* and *s-cis* acrolein, respectively. (b) Excited state molecular orbitals for *s-trans* and *s-cis* acrolein, respectively. Orbitals were tabulated for visualization on a CACHE Scientific, Inc. workstation, Version 3.6.

sition accessed at 199 nm, a series of *ab initio* calculations using the GAUSSIAN 92 set of programs were performed on both *cis* and *trans* acrylic acid. It was found that the previously assigned $\pi \rightarrow \pi^*$ transition centered on the C=C of the vinyl group is in fact a mixed state consisting of both π^* character centered on the C=C bond and a π^* transition centered on the C=O bond. A listing of the relevant molecular orbital coefficients corresponding to the $\pi(C=C) \rightarrow \pi^*(C=C)/\pi^*(C=O)$ transition are given in Table VII. Pictures of the orbitals are given in Fig. 4.

The emission spectrum of gaseous acryloyl chloride at 199 nanometers is shown in Fig. 5 with peak assignments listed in Table VIII. The peaks are assigned according to the Raman lines identified for this compound by Katon and Fairheller¹³ in an earlier experiment involving liquid acryloyl chloride. There have been no extensive studies of the character of electronic transitions in acryloyl chloride, but the emission spectrum is clearly similar to that of acrolein and acrylic acid. There is a progression in the C=C stretch, with peaks corresponding to at least three quanta in the stretch. In addition, as with acrylic acid, we saw peaks corresponding to several quanta in the C=O stretch. This would

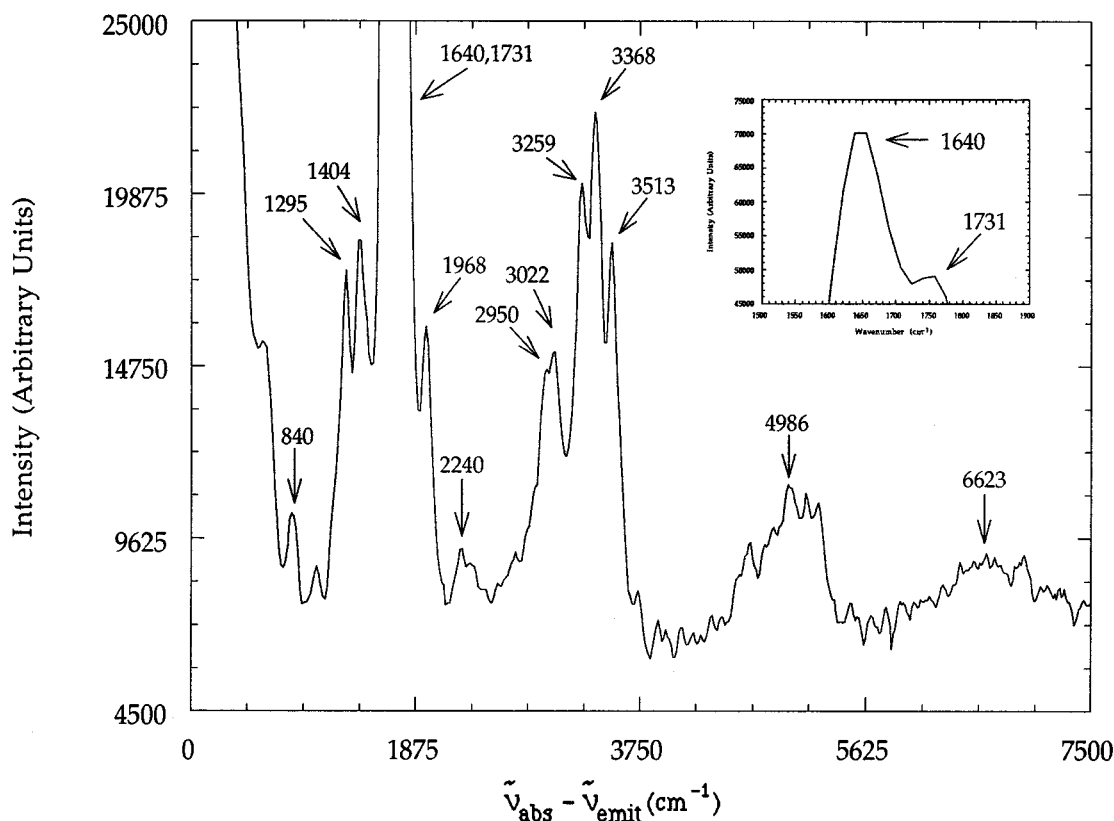


FIG. 3. Emission spectrum of acrylic acid taken at an excitation wavelength of 199 nm. Emission is seen corresponding to progressions in the C=C and C=O stretching overtones and various combination bands. Assignment of peaks is given in Table VI.

suggest that the transition at 199 nm is of similar character to that observed in acrolein and acrylic acid. An interesting feature of the emission spectrum for acryloyl chloride is the existence of a number of combinations bands consisting of several quanta in both the C=C and C=O stretch. The lack of better resolved peaks in the emission spectrum for acrylic acid precludes us from making the same observation, although this by no means rules out that such peaks exist.

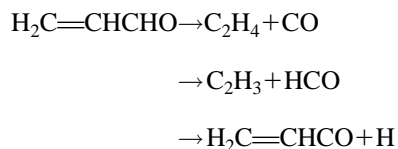
The results of our GAUSSIAN 92 CIS calculations on both the *cis* and *trans* geometries of acryloyl chloride are quite similar to acrolein and acrylic acid. Again, we found that the transition in this region is to a state of mixed $\pi^*(\text{C}=\text{C})/\pi^*(\text{C}=\text{O})$ character. Therefore, one would expect to see quanta in both C=C and C=O stretching progressions and combination bands, as we do in the emission spectrum. A listing of the relevant molecular orbital coefficients obtained from the GAUSSIAN 92 calculations are given in Table IX. Pictures of the orbitals are given in Fig. 6.

V. DISCUSSION

The experimental and *ab initio* electronic structure results presented here suggest that the excited state of the three molecules, acrolein, acrylic acid, and acryloyl chloride, all have a similar electronic state accessed at 199 nm. Although the electronic transition on acrylic acid was assumed to be $\pi\pi^*$ localized on the vinyl group, this work shows that the π^* orbital is of mixed C=C/C=O character similar to that in acrolein. This assignment is further supported by the fact

that the electronic absorption is shifted to the red of that observed for the $\pi\pi^*(\text{C}=\text{C})$ transition in ethylene. Clearly the mixing of the $\pi^*(\text{C}=\text{C})$ and the $\pi^*(\text{C}=\text{O})$ orbital results in a mixing and splitting of the excited state orbital, so one may access the mixed π^* orbital at lower transition energies.

Our interest in these systems goes beyond the nature of the excited state in the Franck-Condon region. While fission of the C-C bond in acrolein produces HCO radical, fission of the C-C bond in acrylic acid produces the reaction intermediate HOCO important in combustion processes. Previous work on the photodissociation of acrolein in a molecular beam conducted at 193 nm^{21,22} show several molecular photodissociation pathways:



including the C-C bond fission direct product HCO. In general, it was shown that all three dissociation pathways produced internally hot products with very little translational energy. Of the total available energy at 193 nm, Haas *et al.*²² show that 87.2% goes into the internal energy of the C₂H₃ and HCO fragments, while the remaining 12.8% is partitioned to translational motion of the photofragments. We are presently investigating the analogous photodissociation pathways of acrylic acid excited at 193 nm.¹ We expect that the

TABLE VI. Acrylic acid emission spectrum peak assignments.

Description	Accepted value ^a in cm ⁻¹	Experimental value ^b in cm ⁻¹
C—H bend, O—H bend	820,861	840
O—H bend, C—C stretch	1280,1295	1295
C—O stretch, C—H bend, CH ₂ scissors	1395,1434	1404
C=C stretch	1637,1660	1640
C=O stretch	1728	1731
2×CH ₂ wag	1954	1968
O—H bend+C—O stretch	2256	2240
2×C—O stretch, 2×CH ₂ scissors	2868	2950
C—H stretch, CH ₂ symmetric stretch	2998,3039	3022
2×C=C stretch	3274	3259
C=C stretch+C=O stretch	3365,3388	3368
2×C=O stretch	3456	3513
Combinations of a total of 3 quanta in the C=C stretch and C=O stretch	4980 (3×C=C)	4986
Combinations of a total of 4 quanta in the C=C stretch and C=O stretch	6640 (4×C=C)	6623

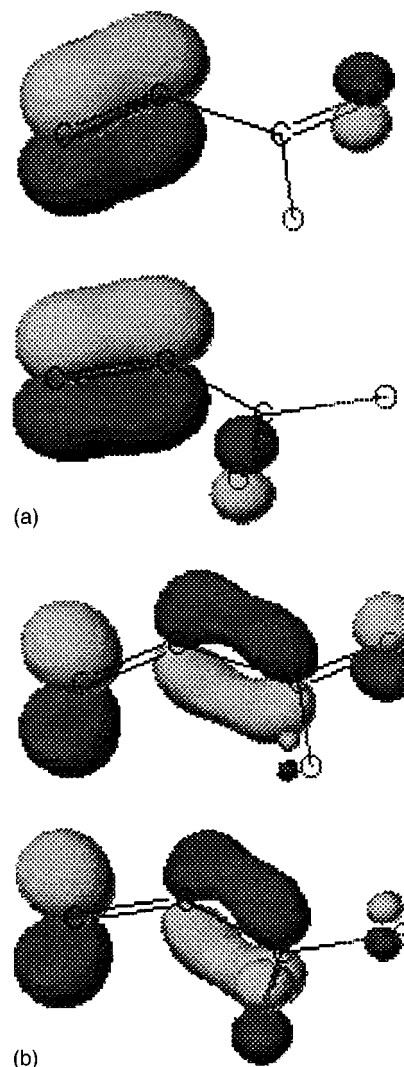
^aFrom Ref. 20.^bOur results given the maximum resolution of 75 cm⁻¹ with current monochromator.

carboxylic acid radical (HOCO) could be found with close to enough internal energy for the reaction $\text{HOCO} \rightarrow \text{OH} + \text{CO}$ to proceed. Preliminary results show that other bond fission channels compete with the production of HOCO from acrylic acid at 193 nm.²³

In general, the photodissociation of compounds with a $\text{C}=\text{C}-\text{C}=\text{O}$ backbone have been shown to produce photofragments with a large percentage of the available en-

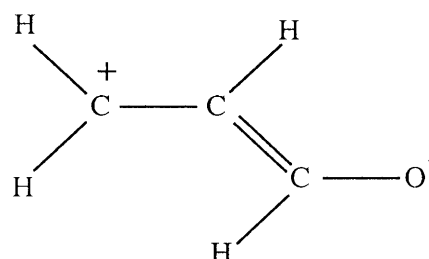
TABLE VII. Molecular orbitals in the 6-31G* basis making the largest contributions to the electronic transitions in acrylic acid ($\text{C}_3\text{H}_3\text{COOH}$) as calculated by GAUSSIAN 92. The molecule is oriented in the XZ plane with the first vinylic carbon atom at the origin.

Atom/atomic orbital	Orbital coefficient ground state	Orbital coefficient excited state
<i>s-trans</i> acrylic acid ($\text{C}_3\text{H}_3\text{COOH}$)		
$\text{C}_1/2p_y$	0.344 30	0.337 24
$\text{C}_1/3p_y$	0.279 15	0.599 49
$\text{C}_2/2p_y$	0.372 69	-0.240 84
$\text{C}_2/3p_y$	0.307 93	-0.437 46
$\text{C}_3/2p_y$	-0.016 90	-0.266 71
$\text{C}_3/3p_y$	-0.026 41	-0.276 81
$\text{O}_1/2p_y$	-0.198 75	0.233 33
$\text{O}_1/3p_y$	-0.164 41	0.277 73
<i>s-cis</i> acrylic acid ($\text{C}_3\text{H}_3\text{COOH}$)		
$\text{C}_1/2p_y$	0.342 05	0.335 77
$\text{C}_1/3p_y$	0.267 06	0.603 68
$\text{C}_2/2p_y$	0.373 37	-0.235 88
$\text{C}_2/3p_y$	0.315 53	-0.436 73
$\text{C}_3/2p_y$	-0.018 24	-0.271 37
$\text{C}_3/3p_y$	-0.028 83	-0.278 49
$\text{O}_1/2p_y$	-0.217 59	0.209 12
$\text{O}_1/3p_y$	-0.176 33	0.266 09

FIG. 4. (a) Ground state molecular orbitals for *s-trans* and *s-cis* acrylic acid, respectively. (b) Excited state molecular orbitals for *s-trans* and *s-cis* acrylic acid, respectively. Orbitals were tabulated for visualization on a CAChe Scientific, Inc. workstation, Version 3.6.

ergy channeled into their internal degrees of freedom and not into their translational motion. The distribution of energy in these systems suggests that their photochemistry at these wavelengths does not proceed through a single direct dissociation mechanism. Rather, it would seem that excitation is initially to a predissociative state from which the dissociation channels are made accessible.

Our *ab initio* calculations for acrolein, are in agreement with previous results of Nagakura,⁷ which showed the existence of a charge-transfer state with the following resonance structure.



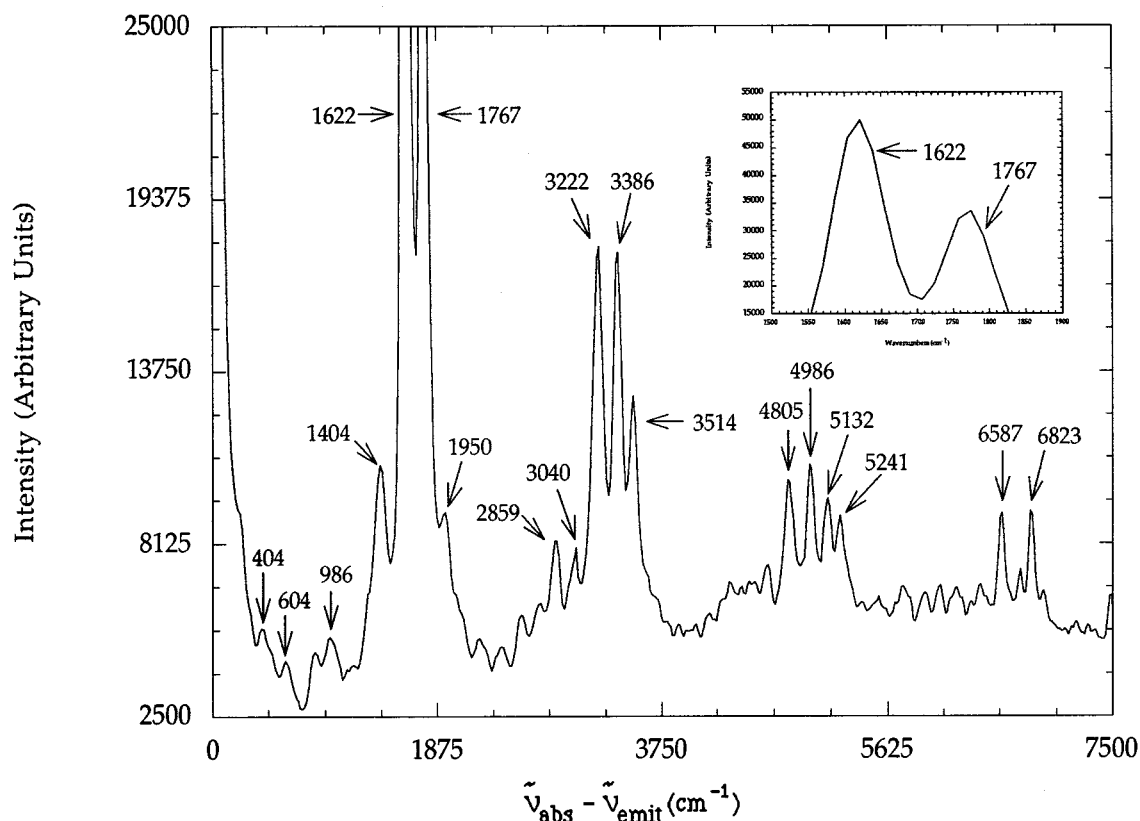


FIG. 5. Emission spectrum of acryloyl chloride taken at an excitation wavelength of 199 nm. Emission is seen corresponding to progressions in the C=C and C=O stretching overtones and various combination bands. Assignment of peaks is given in Table VIII.

TABLE VIII. Acryloyl chloride emission spectrum peak assignments.

Description	Accepted value ^a in cm ⁻¹	Experimental value ^b in cm ⁻¹
C—C=C skeleton	390	404
C—Cl stretch	615	604
CH ₂ twist	980	986
CH ₂ scissors	1399	1404
C=C stretch	1620	1622
C=O stretch	1767	1767
2×CH ₂ twist	1960	1950
2×CH ₂ scissors	2798	2859
CH ₂ symmetric stretch	3041	3040
2×C=C stretch	3240	3222
C=C stretch+C=O stretch	3387	3386
2×C=O stretch	3534	3514
3×C=C stretch	4860	4805
2×C=C stretch+C=O stretch	5007	4986
C=C stretch+2×C=O stretch	5154	5132
3×C=O stretch	5301	5241
3×C=C stretch+C=O stretch	6627	6587
2×C=C stretch+2×C=O stretch	6774	6823

^aFrom Ref. 13.

^bOur results given the maximum resolution of 75 cm⁻¹ with current monochromator.

TABLE IX. Molecular orbitals in the 6-31G* basis making the largest contributions to the electronic transitions in acryloyl chloride (C₂H₃COCl), as calculated by GAUSSIAN 92. The molecule is oriented in the XZ plane with the first vinylic carbon atom at the origin.

Atom/atomic orbital	Orbital coefficient ground state	Orbital coefficient excited state
<i>s-trans</i> acryloyl chloride (C ₂ H ₃ COCl)		
C ₁ /2p _y	0.339 22	0.328 44
C ₁ /3p _y	0.269 18	0.539 46
C ₂ /2p _y	0.379 40	-0.199 14
C ₂ /3p _y	0.311 89	-0.340 61
C ₃ /2p _y	-0.015 85	-0.296 77
C ₃ /3p _y	-0.024 01	-0.357 07
O/2p _y	-0.194 43	0.276 70
O/3p _y	-0.157 67	0.335 81
<i>s-cis</i> acryloyl chloride (C ₂ H ₃ COCl)		
C ₁ /2p _y	0.343 19	0.314 86
C ₁ /3p _y	0.263 90	0.538 76
C ₂ /2p _y	0.380 30	-0.189 93
C ₂ /3p _y	0.317 17	-0.339 77
C ₃ /2p _y	-0.016 41	-0.308 99
C ₃ /3p _y	-0.024 93	-0.369 53
O/2p _y	-0.201 06	0.264 65
O/3p _y	-0.160 13	0.336 35

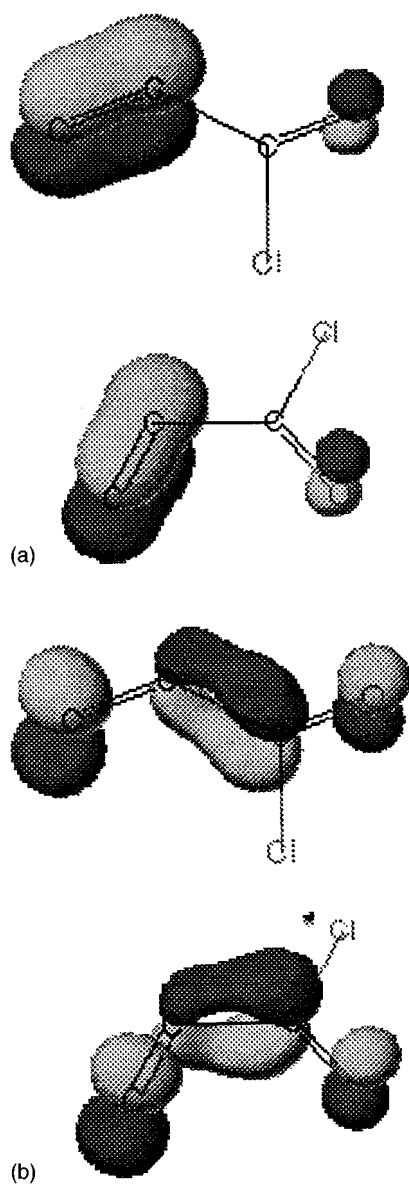


FIG. 6. (a) Ground state molecular orbitals for *s-trans* and *s-cis* acryloyl chloride, respectively. (b) Excited state molecular orbitals for *s-trans* and *s-cis* acryloyl chloride, respectively. Orbitals were tabulated for visualization on a CAChe Scientific, Inc. workstation, Version 3.6.

The excited state geometry differs greatly from the ground state geometry in that the alternating double bond–single bond–double bond structure of the ground state is interchanged with the excited state single bond–double bond–single bond structure. This drastic change in the geometry of the excited state basically closes off the direct dissociation

mechanism that would lead to C–C bond fission in any of the three molecules (acrolein, acrylic acid, and acryloyl chloride). Therefore, the state accessed at this wavelength is to a predissociative state and not to a state repulsive in the C–C bond in the Franck–Condon region.

In general, from the emission spectroscopy experiments and the *ab initio* calculations, the transition at 199 nm in acrolein, acrylic acid, and acryloyl chloride can be classified as a $\pi \rightarrow \pi^*$ transition on both C=C and C=O chromophores. Further studies involving molecular beam dissociation experiments may help in further determining the dynamics of these molecules as they photodissociate into their respective photofragments.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, under Grant No. DE-FG02-92ER14305. L.J.B. gratefully acknowledges the support of an Alfred P. Sloan Research Fellowship.

- ¹J. T. Petty, J. A. Harrison, and C. B. Moore, *J. Phys. Chem.* **97**, 11194 (1993).
- ²B. Lewis and G. v. Elbe, *Combustion, Flames and Explosion of Gases* (Academic, New York, 1961), p. 90.
- ³P. M. Banks and N. G. Kockarts, *Aeronomy* (Academic, New York, 1973), p. 362.
- ⁴E. J. Heller, *J. Chem. Phys.* **68**, 3891 (1978); S. Y. Lee and E. J. Heller, *ibid.* **71**, 4777 (1979).
- ⁵D. Imre, J. L. Kinsey, A. Sinha, and J. Krenos, *J. Phys. Chem.* **88**, 3956 (1984).
- ⁶A. D. Walsh, *Trans. Faraday Soc.* **42**, 66 (1946).
- ⁷S. Nagakura, *Mol. Phys.* **3**, 105 (1960).
- ⁸H. Morita, K. Fuke, and S. Nagakura, *Bull. Chem. Soc. Jpn.* **49**, 922 (1976).
- ⁹T. Ukaji, *Bull. Chem. Soc. Jpn.* **32**, 1266 (1959).
- ¹⁰For information on sum frequency generation in BBO, see: W. L. Glab and J. P. Hessler, *Appl. Opt.* **26**, 3181 (1987).
- ¹¹R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.* **26**, 634 (1957).
- ¹²K. Bolton, N. L. Owen, and J. Sheridan, *Nature* **218**, 266 (1968); N. L. Owen, *J. Mol. Struct.* **6**, 37 (1970).
- ¹³W. R. Fairheller and J. E. Katon, *J. Chem. Phys.* **47**, 1248 (1967).
- ¹⁴GAUSSIAN 92, Revision C, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburg, PA, 1992.
- ¹⁵K. Bolton, D. G. Lister, and J. Sheridan, *J. Chem. Soc. Faraday Trans. 2* **70**, 113 (1974).
- ¹⁶R. Kewley, D. C. Hemphill, and R. F. Curl, Jr., *J. Mol. Spectrosc.* **44**, 443 (1972).
- ¹⁷E. A. Cherniak and C. C. Costain, *J. Chem. Phys.* **45**, 104 (1966).
- ¹⁸K. Hagen and K. Hedberg, *J. Am. Chem. Soc.* **106**, 6150 (1984).
- ¹⁹R. K. Harris, *Spectrochim. Acta* **20**, 1129 (1964).
- ²⁰W. R. Fairheller and J. E. Katon, *Spectrochim. Acta A* **23**, 2225 (1967).
- ²¹H. Shinohara and N. Nishi, *J. Chem. Phys.* **77**, 234 (1982).
- ²²B.-M. Haas, T. K. Minton, P. Felder, and J. R. Huber, *J. Phys. Chem.* **95**, 5149 (1991).
- ²³D. C. Kitchen, M. F. Arendt, B. Hu, and L. J. Butler (unpublished).