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Product Branching Ratio of the HCCO + NO Reaction

Kwang Taeg Rim[†] **and John F. Hershberger***

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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The reaction of HCCO radicals with NO was studied at room temperature by excimer laser photolysis of ketene precursor molecules followed by infrared absorption spectroscopic detection of CO and CO_2 product molecules. After quantification of product yields and consideration of secondary chemistry, we obtain the following product branching ratios (1σ error bars) at 296 K: 0.12 ± 0.04 for CO_2 + (HCN) and 0.88 ± 0.04 for CO + (HCNO). In addition, we estimate a relative quantum yield for HCCO production in the 193 nm photolysis of CH_2CO to be 0.17 ± 0.02.

Introduction

The spectroscopy[1−4] and kinetics[4−8] of the ketenyl radical (HCCO) is of recent interest, partly because of the role this species plays in combustion chemistry. HCCO is formed in flames primarily by the oxidation of acetylene.[9,10] It has been observed in laboratory studies by infrared absorption[4] and laser-induced fluorescence spectroscopy.[1,2] Several kinetic studies involving HCCO have appeared recently, with total rate constant measurements reported for reactions with NO,[4−7] NO_2,[5] O_2,[5] O,[8] and C_2H_2.[5] The reaction with NO is of particular interest because of the role it plays in NO-reburning mechanisms[11−15] for the reduction of NO_x emissions from fossil-fuel combustion processes. Several product channels are possible:

$$\mathrm{HCCO + NO \rightarrow CO_2 + (HCN)} \qquad \Delta H^\circ = -527.2\ \mathrm{kJ/mol} \tag{1a}$$

$$\mathrm{\rightarrow CO + (HCNO)} \qquad \Delta H^\circ = -200.8\ \mathrm{kJ/mol} \tag{1b}$$

$$\mathrm{\rightarrow NCO + HCO} \qquad \Delta H^\circ = -71.1\ \mathrm{kJ/mol} \tag{1c}$$

The thermochemistry shown is for HCN and HCNO, but several other isomers of these species represent possible, albeit unlikely, product channels as well. Several reports of the total rate constant of this reaction have appeared. Unfried et al. used infrared absorption near 2023 cm^{-1} to detect HCCO and reported $k_1 = (3.9 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[4] Temps et al. used far-infrared laser magnetic resonance to detect HCCO and obtained $(2.2 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[5] Boullart et al. used discharge flow-mass spectrometry to obtain $k_1 = (1.0 \pm 0.3) \times 10^{-10}$ exp [-350 ± 150)/T] cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290−670 K and also reported the following product branching ratios at 700 K: $\phi_{1a} = 0.23 \pm 0.09$, $\phi_{1b} = 0.77 \pm 0.09$.[6] These data are contradicted by recent calculations and flow reactor studies. Miller et al. used statistical theories and a QCISD potential surface of Nguyen et al.[7] to predict $\phi_{1a} = 0.81$ at 300 K, with a moderate temperature dependence, decreasing to about 0.32 at 2000 K.[12] Kinetic modeling of flow reactor experiments at 1100−1400 K were best fit by a branching ratio of $\phi_{1a} = 0.65$.[13]

Measurement of the product branching ratio of the title reaction represents a challenge because no ideal photolytic source of HCCO is known. Typically, previous experiments have used the reaction of oxygen atoms with acetylene to form HCCO:

$$\mathrm{O + C_2H_2 \rightarrow HCCO + H} \tag{2a}$$

$$\mathrm{\rightarrow CH_2 + CO} \tag{2b}$$

This approach has two problems: reaction 2 is quite slow at moderate temperatures,[8,9] and the presence of channel 2b complicates quantification of product yields. Unfried et al., however, reported that direct photolysis of ketene at 193 nm produces ketenyl radicals as well as the well-known methylene + CO channel:[4]

$$\mathrm{CH_2CO} + h\nu\ (193\ \mathrm{nm}) \rightarrow \mathrm{CH_2 + CO} \tag{3a}$$

$$\mathrm{\rightarrow HCCO + H} \tag{3b}$$

We have chosen this approach in the experiments reported here. Reaction 3b represents a faster source of HCCO than (2a), although we must still contend with the production of CH_2 + CO in channel 3a.

Experimental Section

The experimental procedure is similar to that described in previous publications.[16,17] A schematic of the experimental apparatus is shown in Figure 1. Photolysis light of 193 nm was provided by an excimer laser (Lambda Physik, Compex 200). Several lead salt diode lasers (Laser Photonics, Analytics Division) operating in the 80−110 K temperature range were used to provide tunable infrared probe laser light. The IR beam was collimated by a lens and combined with the UV light by means of a dichroic mirror, and both beams were copropagated through a 1.46 m absorption cell. After the UV light was removed by a second dichroic mirror, the infrared beam was then passed into a ¼ m monochromator and focused onto a 1 mm InSb detector (Cincinnati Electronics, ~1 μs response time). Transient infrared absorption signals were recorded on a LeCroy 9310A digital oscilloscope and transferred to a computer for analysis.

[†] Current address: Department of Chemistry, Columbia University, 3000 Broadway MS 3109, New York, NY 10027.

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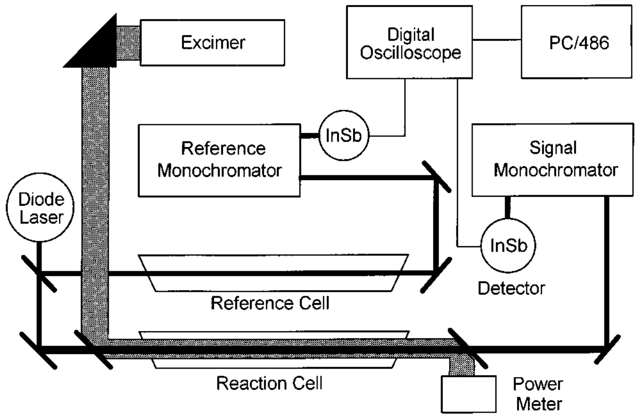

Figure 1. Schematic of the experimental apparatus.

SF_6, Xe, and CF_4 (Matheson) were purified by repeated freeze−pump−thaw cycles at 77 K. A trace of CO_2 was removed from SF_6 by the use of an ascarite trap. NO (Matheson) and $^{15}N^{18}O$ (Isotec) were purified by repeated freeze−pump−thaw cycles at 163 K to remove NO_2 and N_2O. Ketene was synthesized by the pyrolysis of acetic anhydride at 700 °C and purified by freeze−pump−thaw cycles at 77 K. The purity of the ketene samples was checked by FTIR. A substantial CO_2 impurity in the ketene sample was observed, and attempts to remove this using ascarite were unsuccessful, apparently due to the reactivity of ketene. The use of labeled $^{15}N^{18}O$ reagents to produce $^{16}O^{12}C^{18}O$ products in the title reaction minimized (but not completely eliminated) interference from this static CO_2 impurity. Note that only the oxygen labeling is important in the experiments reported here. Furthermore, isotopically labeled NO was not used for the CO detection experiments, because channel 1b would probably produce $HC^{15}N^{18}O$ + CO, and not $C^{18}O$.

CO, N_2O, and isotopically labeled $^{16}O^{12}C^{18}O$ product molecules were probed by observing the following absorption lines:

$$CO\ (v = 1 \leftarrow v = 0) \qquad P(8),\ 2111.543\ cm^{-1}$$

$$N_2O\ (00^01) \leftarrow (00^00) \qquad P(13),\ 2212.326\ cm^{-1}$$

$$^{16}O^{12}C^{18}O\ (00^01) \leftarrow (00^00) \qquad R(13),\ 2341.812\ cm^{-1}$$

The HITRAN molecular database was used to locate and identify the spectral lines of product molecules.[18] The spectral lines used are near the peak of the rotational Boltzmann distribution, minimizing sensitivity to small heating effects. For CO_2 product molecule measurements, the infrared laser beam path was purged with N_2 to remove atmospheric CO_2.

Typical experimental conditions were $P_{CH_2CO} = 0.1$ Torr, $P_{SF_6} = 2.0$ Torr, $P_{CF_4} = 3.0$ Torr, and $P_{NO} = 0-0.4$ Torr. Typically, several (two to five) laser shots were averaged when probing the weaker CO_2 signals, but no signal averaging was used for the stronger CO signals.

Results

Time-resolved transient absorption signals of product molecules at 296 K are shown in Figure 2. The CO transient signals were produced by the photolysis of CH_2CO in the presence of NO reagents and CF_4 buffer gas. CO signals were also observed in the absence of NO reagent and are attributed to direct ketene photolysis, channel 3a.

The $^{16}O^{12}C^{18}O$ transient signals were obtained by photolyzing CH_2CO in the presence of labeled $^{15}N^{18}O$ and SF_6 buffer gas (no signals were obtained in the absence of $^{15}N^{18}O$). The CO_2 impurity in the ketene samples produced some interference even when probing $^{16}O^{12}C^{18}O$ due to the ^{18}O natural abundance. This factor as well as the small CO_2 product yields are responsible for the poor S/N of the CO_2 signals. Typical changes in transmittance ($\Delta I/I_0$) values are 10−15% for the CO transient signals but only 1−2% for $^{16}O^{12}C^{18}O$ signals.

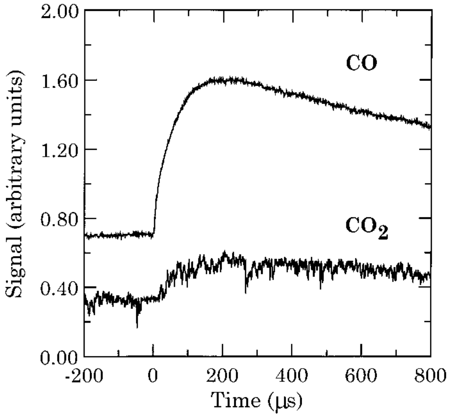

Figure 2. Transient infrared absorption signals for CO and CO_2 product molecules. CO transients were obtained from a single photolysis laser shot. CO_2 transients were averages of two photolysis laser shots. Reaction conditions: $P_{CH_2CO} = 0.1$ Torr, $P_{NO} = 0.2$ Torr, $P_{Xe} = 1.0$ Torr, $P_{SF_6} = 2.0$ Torr (CO_2 signals only), $P_{CF_4} = 3.0$ Torr (CO signals only).

Previous experiments in our laboratory[16,19] as well as vibrational energy transfer measurements[20−23] have demonstrated that SF_6 is an efficient buffer gas for the relaxation of vibrationally excited CO_2 or N_2O to a Boltzmann distribution but that CF_4 is a more efficient relaxer of vibrationally excited CO. The relatively slow rise times observed in the transient signals represent a convolution of the fast reaction rate k_1 with slower vibrational relaxation rates. In any case, the vibrational populations are relaxed to a Boltzmann distribution within 100−200 μs. The slow ~1 ms decay is attributed to diffusion of product molecules out of the probed region of the reaction cell.

Attempts to detect N_2O product molecules in this reaction system were unsuccessful. If channel 1c is active, one expects N_2O formation in high yield via the secondary reaction:

$$NCO + NO \rightarrow N_2O + CO \qquad (4a)$$

$$\rightarrow CO_2 + N_2 \qquad (4b)$$

Previous experiments have shown that $\phi_{4a} = 0.44$ at 298 K.[16] Our failure to detect N_2O indicates that channel 1c does not contribute significantly to the title reaction. This is a more sensitive test for channel 1c than direct NCO detection by infrared spectroscopy[24] because N_2O has much greater infrared line strengths.

Absorption signals were converted to number densities using tabulated line strengths[14] and equations described previously.[16] The line strength of R(13) of $^{16}O^{12}C^{18}O$ was obtained by dividing the tabulated line strength, $S_{vj} = 6.632 \times 10^{-21}$ (which assumes a natural abundance sample), by the isotopic abundance of $^{16}O^{12}C^{18}O$, 3.947×10^{-3}. The product yields of CO and $^{16}O^{12}C^{18}O$ are shown in Figure 3 as a function of reagent NO pressure. As shown, significant amounts of CO are formed in the direct photolysis of ketene at 193 nm via channel 3a. Upon addition of NO to the reaction mixture, however, a significant and reproducible increase in the CO yield is observed due to reaction 1b. In addition, a small but significant yield of $^{16}O^{12}C^{18}O$ was observed when $^{15}N^{18}O$ was included in the

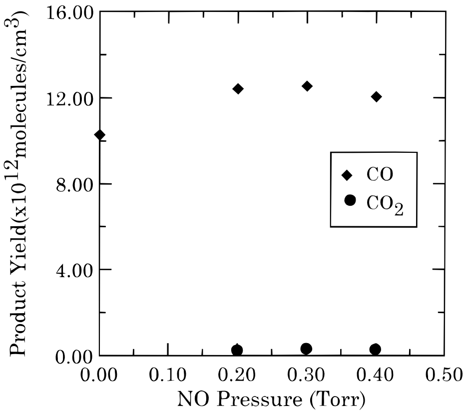

Figure 3. Product yields of CO and CO_2 product molecules are shown as a function of NO pressure. Experimental conditions are identical to those of Figure 2. Filled triangles: CO yield. Filled circles: CO_2 yields. Reaction conditions: $P_{CH_2CO} = 0.1$ Torr, $P_{NO} = 0-0.4$ Torr, $P_{Xe} = 1.0$ Torr, $P_{SF_6} = 2.0$ Torr (CO_2 only), $P_{CF_4} = 3.0$ Torr (CO only).

TABLE 1: Product Branching Ratio of the HCCO + NO Reaction at 296 K[a]

product channel	branching ratio without Xe	branching ratio with Xe
CO + (HCNO)	0.84 ± 0.07	0.88 ± 0.04
CO_2 + (HCN)	0.16 ± 0.07	0.12 ± 0.04

[a] Error bars represent one standard deviation.

TABLE 2: Relative Branching Ratio for the Photolysis of CH_2CO at 193 nm[a]

product channel	branching ratio without Xe	branching ratio with Xe
CH_2 + CO	0.84 ± 0.02	0.83 ± 0.02
HCCO + H	0.16 ± 0.02	0.17 ± 0.02

[a] Error bars represent one standard deviation.

reaction mixture. The product yields are essentially unchanged over the range 0.2−0.4 Torr of NO, indicating that under these conditions virtually all of the HCCO radicals formed in (1a) are removed by reaction with NO.

If only reactions 1 and 3 are considered, the branching ratio of reaction 1 may be calculated as follows. We define $[CO]_0$ as the CO yield observed in the absence of NO, i.e., that produced by (3a). Let $[CO]_{tot}$ be the total CO yield observed in the presence of NO. The difference $[CO]_{dif} = [CO]_{tot} - [CO]_0$ is the CO yield from channel 1b of the title reaction. If we assume that only channels 1a and 1b are active, the product branching ratio ϕ_{1b} is then $[CO]_{dif}/([CO]_{dif} + [CO_2])$, and $\phi_{1a} = 1 - \phi_{1b}$. Table 1 shows the results of this analysis, averaged over nine different measurements.

An additional piece of information that can be obtained from our data is the relative photodissociation quantum yields of channels 3a and 3b in the 193 nm ketene photolysis. Let $x = [CO]_{tot}/[CO]_0 - 1$. Since $[CO]_{tot}/[CO]_0 = ([CO]_0 + [HCCO]_0\phi_{1b})/[CO]_0$, we have

$$x = [HCCO]_0\phi_{1b}/[CO]_0 \tag{5}$$

The relative quantum yields for CO and HCCO formation in the photolysis of ketene are $\phi_{3a} = [CO]_0/([CO]_0 + [HCCO]_0)$ and $\phi_{3b} = [HCCO]_0/([CO]_0 + [HCCO]_0)$, respectively. By solving eq 5 for $[CO]_0$ and substituting, we obtain $\phi_{3a} = \phi_{1b}/(x + \phi_{1b})$ and $\phi_{3b} = 1 - \phi_{3a}$. Note that these are only relative quantum yields, as we do not know the fluorescence quantum yield of ketene at 193 nm. The result of this analysis is shown in Table 2. It is apparent that ketenyl radical formation is a relatively minor but not insignificant channel in the photolysis of ketene and that the more well-known CH_2 + CO channel dominates the photolysis. This fact is partly responsible for the large background $[CO]_0$ in this study.

TABLE 3: Collisional Quenching of $^1CH_2$ and ^1NH

reaction	rate const, cm^3 molecule^{-1} s^{-1}	ref
$^1CH_2$ + He	2.5×10^{-12}	34
$^1CH_2$ + Ar	$(4.8-5.2) \times 10^{-12}$	32, 34
$^1CH_2$ + N_2	7.0×10^{-12}	34
^1NH + N_2	7.9×10^{-14}	35
^1NH + Xe	1.1×10^{-11}	35

Discussion

The above analysis is dependent on the assumption that only reactions 1 and 3 are important sources of CO or CO_2 when CH_2CO/NO/buffer gas mixtures are photolyzed. Several secondary reactions must be considered. Some of these are quite slow:

$$H + CH_2CO \rightarrow \text{products} \tag{6}$$

$$^3CH_2 + CH_2CO \rightarrow \text{products} \tag{7}$$

where $k_6 = 6.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_7 < 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[25,26] Although CO is a likely product of both of these reactions, under our experimental conditions of 0.1 Torr of CH_2CO, these reactions occur on time scales of >1 ms, which is much greater than the observed transient signal rise times of ∼100 μs and, in fact, is comparable to or slower than the time scale for diffusion of products out of the probed volume. Thus, these reactions have little effect on our results.

A faster secondary reaction is

$$^3CH_2 + NO \rightarrow HCNO + H \tag{8}$$

where $k_8 = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[27] Although other product channels than shown are possible in reaction 8, HCNO formation has been previously identified as the dominant product.[28,29] This reaction will therefore not significantly affect our measured CO or CO_2 yields.

A further issue is the possibility of excited singlet state methylene production in the photolysis of ketene. $^1CH_2$ production in high yield is well-known in the near-UV photolysis of ketene near 300 nm,[30] but to our knowledge the relative amount of $^1CH_2$ vs $^3CH_2$ formation at 193 nm has not been reported. If $^1CH_2$ is a major component of 3a, then several fast reactions are possible:

$$^1CH_2 + CH_2CO \rightarrow \text{products} \tag{9}$$

$$^1CH_2 + NO \rightarrow \text{products} \tag{10}$$

where $k_9 = (2.0-2.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_{10} = 1.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.[31,32] Either of these reactions could form CO. To test for these possibilities, we performed some experiments with an excess of xenon included in the reaction mixture in order to electronically relax any $^1CH_2$ formed:

$$^1CH_2 + Xe \rightarrow {}^3CH_2 + Xe \tag{11}$$

Unfortunately, no rate constants for reaction 11 have been reported. For comparison, Table 3 shows literature values of kinetic data for removal of $^1CH_2$ as well as the isoelectronic species NH($^1\Delta$) with several collision partners.[31−35] As shown, Xe is a faster relaxer of NH($^1\Delta$) than N_2 by more than 2 orders of magnitude. This is presumably due to the well-known heavy atom effect in promoting spin-forbidden processes. Similar effects are expected to be present in singlet methylene relaxation processes as well. Although explicit experimental data would clearly be desirable, it is likely than reaction 11 occurs with a large rate constant, probably at least an order of magnitude greater than the $^1CH_2 + Ar$ value of 5.2×10^{-12} cm^3 molecule^{-1} s^{-1}. Addition of Xe to our reaction mixtures is therefore expected to be effective in relaxing $^1CH_2$.

Tables 1 and 2 show data obtained both with and without 1.0 Torr of xenon in the reaction mixture. As shown, the measured branching ratios of the title reaction were only very slightly affected by the addition of Xe. Several interpretations of this result are possible. One is that the $^1CH_2$ yield in the 193 nm photolysis of ketene is small. It is more likely, however, that $^1CH_2$ is in fact produced in our system but is efficiently relaxed even in the absence of Xe, possibly by nonreactive channels of (9) or (10) or by collisions with CF_4 or SF_6 buffer gas. In any case, our data show that secondary chemistry of $^1CH_2$ only has a minor effect on our results. We believe that the data obtained with Xe included are the more reliable.

Comparing our results with the previously reported values, we are in reasonable agreement with the study of Boullart et al., which reported $\phi_{1a} = 0.23 \pm 0.09$ and $\phi_{1b} = 0.77 \pm 0.09$ at 700 K.[6] Our results are in marked disagreement, however, with more recent calculations[12] and modeling studies,[13,15] which have suggested that $\phi_{1a} = 0.81$ at 300 K and decreases moderately with temperature. The potential energy surface of this reaction[7] involves initial formation of an HC(NO)CO adduct. Formation of (1b) proceeds through a C−C bond fission, while a four-centered cyclic intermediate is involved in the route to channel (1a). These pathways are comparable to similar pathways in the potential surface of the isoelectronic NCO + NO reaction, which produces $N_2O + CO$ and $N_2 + CO_2$ in comparable yield.[16] Our results and those of ref 6 suggest, however, that the HCCO + NO potential surface is not known with sufficient accuracy to quantitatively predict the branching ratio.

Conclusion

Photolysis (193 nm) of ketene was used to investigate the reaction of HCCO radicals with NO. By detection of CO and CO_2 products and consideration of possible secondary chemistry, we find that CO + (HCNO) is the major product channel, with a branching ratio of 0.88 ± 0.04, and that CO_2 + (HCN) is a minor channel, with a branching ratio of 0.12 ± 0.04.

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References and Notes

(1) Brock, L. R.; Mischler, B.; Rohlfing, E. A.; Bise, R. T.; Neumark, D. M. *J. Chem. Phys.* **1997**, *107*, 665.
(2) Brock, L. R.; Mischler, B.; Rohlfing, E. A. *J. Chem. Phys*. **1999**, *110*, 6773.
(3) Osborn, D. L.; Mordaunt, D. H.; Choi, H.; Bise, R. T.; Neumark, D. M.; Rohlfing, C. M. *J. Chem. Phys.* **1996**, *105*, 10087.
(4) Unfried, K. G.; Glass, G. P.; Curl, R. F. *Chem. Phys. Lett.* **1991**, *177*, 33.
(5) Temps, F.; Wagner, H. Gg.; Wolf, M. *Z. Phys. Chem*. **1992**, *176*, 27.
(6) Boullart, W.; Ngugen, M. T.; Peeters, J. *J. Phys. Chem*. **1994**, *98*, 8036.
(7) Nguyen, M. T.; Boullart, W.; Peeters, J. *J. Phys. Chem*. **1994**, *98*, 8030.
(8) Peeters, J.; Boullart, W.; Devriendt, K. *J. Phys. Chem*. **1995**, *99*, 3583.
(9) Vinckier, C.; Schaekers, M.; Peeters, J. *J. Phys. Chem.* **1985**, *89*, 508.
(10) Schmoltner, P. M.; Chu, P. M.; Lee, Y. T. *J. Chem. Phys*. **1989**, *91*, 5365.
(11) Chen, S. L.; McCarthy, J. M.; Clark, W. D.; Heap, M. P.; Seeker, W. R.; Pershing, D. W. *Symp. (Int.) Combust Proc*. **1986**, *21*, 1159.
(12) Miller, J. A.; Durant, J. L.; Glarborg, P. *Symp. (Int.) Combust. Proc*. **1998**, *27*, 235.
(13) Glarborg, P.; Alzueta, M. U.; Dam-Johansen, K.; Miller, J. A. *Combust. Flame* **1998**, *115*, 1.
(14) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287.
(15) Prada, L.; Miller, J. A. *Combust. Sci. Technol*. **1998**, *132*, 225.
(16) Cooper, W. F.; Park, J.; Hershberger, J. F. *J. Phys. Chem*. **1993**, *97*, 3283.
(17) Rim, K. T.; Hershberger, J. F. *J. Phys. Chem*. *A* **1998**, *102*, 5898.
(18) Rothman, L. S.; et al. *J. Quant. Spectrosc. Radiat. Transfer* **1992**, *48*, 469.
(19) Cooper, W. F.; Hershberger, J. F. *J. Phys. Chem*. **1992**, *96*, 771.
(20) Fakhr, A.; Bates, R. D., Jr. *Chem. Phys. Lett*. **1980**, *71*, 381.
(21) Stephenson, J. C.; Moore, C. B. *J. Chem. Phys*. **1970**, *52*, 2333.
(22) Richman, D. C.; Millikan, R. C. *J. Chem. Phys*. **1975**, *63*, 2242.
(23) Green, W. H.; Hancock, J. K. *J. Chem. Phys*. **1973**, *59*, 4326.
(24) Brueggemann, R.; Petri, M.; Fischer, H.; Mauer, D.; Reinert, D.; Urban, W. *Appl. Phys. B* **1989**, *48*, 105.
(25) Michael, J. V.; Nava, D. F.; Payne, W. A.; Stief, L. J. *J. Phys. Chem* **1979**, *70*, 5222.
(26) Darwin, D. C.; Moore, C. B. *J. Phys. Chem*. **1995**, *99*, 13467.
(27) Darwin, D. C.; Moore, C. B. *J. Phys. Chem*. **1989**, *93*, 1074.
(28) Bauerle, S.; Klatt, M.; Wagner, H. Gg. *Ber Bunsen-Ges. Phys. Chem*. **1995**, *99*, 97.
(29) Grussdorf, J.; Temps, F.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem*. **1997**, *101*, 134.
(30) Okabe, H. *Photochemistry of Small Molecules*; J. Wiley: New York, 1978; p 310.
(31) Langford, A. O.; Petek, H.; Moore, C. B. *J. Chem. Phys*. **1983**, *78*, 6650.
(32) Hancock, G.; Heal, M. R. *J. Phys. Chem*. **1992**, *96*, 10316.
(33) Hayes, F.; Lawrance, W. D.; Staker, W. S.; King, K. D. *J. Phys. Chem*. **1996**, *100*, 11314.
(34) Wagener, R. *Z. Naturforsch*. **1990**, *45a*, 649.
(35) Nelson, H. H.; McDonald, J. R.; Alexander, M. H. *J. Phys. Chem.* **1990**, *94*, 3291.