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Time-Resolved Infrared Study on the Photochemistry of *O*-Fluoroformyl- and *O*-Chlorooxalyl-9-fluorenone Oxime: The Reactivity of the Fluoroformyl Radical in Acetonitrile Solution

Götz Bucher,* Christoph Kolano,*,† Olaf Schade, and
Wolfram Sander

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum,
Universitätsstr. 150, D-44801 Bochum, Germany

goetz.bucher@rub.de; c.kolano@pci.unizh.ch

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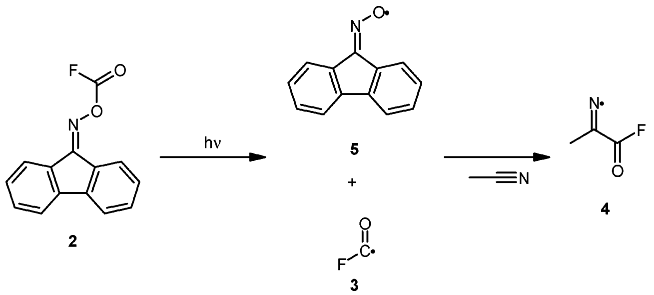

This note describes the photochemistry of *O*-chlorooxalyl- and *O*-fluoroformyl-9-fluorenone oxime. The solution photochemistry of both precursors was investigated by time-resolved step/scan FTIR spectroscopy. Experiments on *O*-chlorooxalyl-9-fluorenone oxime only allowed for detection of CO_2 and bleaching of the precursor, indicating predominant N−O cleavage. The chlorocarbonyl radical, $ClCO^{\bullet}$, was not detected. In contrast, TRIR investigations on fluoroformyl oxime **2** gave evidence for formation of the fluoroformyl radical $FCO^{\bullet}$ (**3**), which rapidly adds to the solvent acetonitrile, yielding a fluoroformyl-functionalized iminyl radical **4**. Its reaction with triplet molecular oxygen, on the other hand, is impeded by an activation enthalpy that has been calculated as $\Delta H^{\#} = 3.2$ kcal/mol.

Oxime derivatives, R═N−O−R′, show a complex photochemistry. This results from photochemical reactions occurring from both singlet and triplet excited states. The most important decay channel usually is cleavage of the N−O bond, which yields a reactive iminyl radical $R{=}N^{\bullet}$, but other reaction mechanisms, including biphotonic photo Beckmann rearrangement, are also observed.[1]

If R′ is an acyl substituent, the acyloxy radical formed in the N−O cleavage reaction will in most cases decarboxylate within less than a nanosecond, yielding a second radical plus carbon dioxide. Thus, photolysis of oxime derivatives represents an attractive entry point to free-radical chemistry. In comparison to other free-radical sources, such as esters derived from *N*-hydroxy-pyridine-2-thione ("Barton-esters"), their main advantage lies in their much higher thermal stability. In particular, esters of 9-fluorenone oxime, with their yellow color and a corresponding convenient long-wavelength absorption, have recently received attention as photochemical sources of a variety of free radicals, among them the benzoyl radical,[2] alkoxycarbonyl radicals,[3] aroyloxy radicals,[4] the selenocysteinyl radical,[5] and even triplet nitrenes.[6] To generate additional novel acyl radical species by photolysis of esters of 9-fluorenone oxime, we embarked on the synthesis and investigation of esters **1** and **2**, which were designed to yield either the fluoroformyloxy radical $F{-}C(O){-}O^{\bullet}$ or the halocarbonyl radicals $X{-}C(O)^{\bullet}$ (X = F or Cl), by N−O or O−C cleavage. Although some of these radicals had previously been investigated by theoretical methods or characterized in an argon matrix or in the gas phase,[8−15] no direct spectroscopic or kinetic information about their solution chemistry had been available so far.

The precursors **1**[7] and **2** were synthesized in a straightforward way by reaction of 9-fluorenone oxime with an excess of oxalyl chloride or monofluorophosgene in dry ether or CCl_4 (Scheme 1).

Their photochemistry was investigated using step/scan time-resolved infrared spectroscopy, employing the third (355 nm) or fourth (266 nm) harmonic of an Nd:YAG laser as an excitation light source and using tetrachloromethane or acetonitrile as solvents. In the case of the chlorooxalyl oxime **1** (λ_{exc} = 355 nm, CCl_4), we observed bleaching of the precursor carbonyl band at $\tilde{\nu} = 1790\ cm^{-1}$ and the formation of CO_2 at $\tilde{\nu} = 2338\ cm^{-1}$ (see Supporting Information). Both processes were instantaneous on our experimental time scale. No transient was observed under an argon atmosphere. Formation of the chloroformyl radical[8−10] thus is not likely to be a major reaction pathway in the photochemistry of **1**, or it is too short lived under our experimental conditions. This is confirmed by the fact that

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[†] Present address: Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland.

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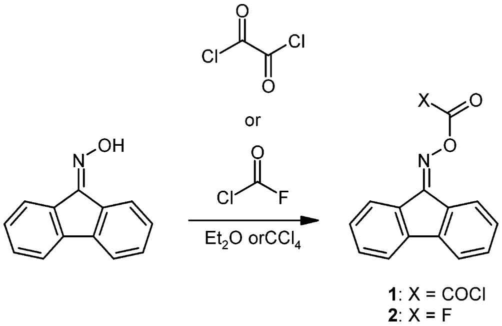
SCHEME 1. **Synthesis of *O*-Haloformyl-9-fluorenone Oximes**



$\nu_{C=O}$ of phosgene (1831 cm^{-1} exptl; 1830 cm^{-1} calcd, B3LYP/6-31G*, frequency scaled by 0.9614) was not detected as a product IR band.

The photochemistry of fluoroformyl oxime **2** was initially also investigated using $\lambda_{exc} = 355$ nm excitation and tetrachloromethane as solvent. Under these conditions, however, the photochemical cleavage of **2** obviously occurred only in poor quantum yield. No transient infrared absorptions of sufficient intensity were detected. We therefore performed the experiments with **2** in acetonitrile, employing $\lambda_{exc} = 266$ nm as the excitation wavelength.

Upon laser flash photolysis ($\lambda_{exc} = 266$ nm, CH_3CN, 1 atm Ar or 1 atm oxygen) of the fluoroformyl oxime **2**, we observed bleaching of the precursor at $\tilde{\nu} = 1857$ cm^{-1} and formation of CO_2 at $\tilde{\nu} = 2338$ cm^{-1}. Both the bleaching and CO_2 formation occurred within the rise time of the experimental setup. No secondary evolution of CO_2 was observed. In addition, we detected a short-lived transient (**A**) ($\tau = 3.3 \pm 0.7$ μs) at $\tilde{\nu} = 1832$ cm^{-1} and a transient with $\tilde{\nu} = 1825$ cm^{-1} (**B**) growing in with a lifetime of $\tau = (1.8 \pm 0.9)$ μs and subsequently decaying with a lifetime of $\tau = (5.0 + 0.7)$ μs (Figures 1 and 2). Because of the complex kinetics at $\tilde{\nu} = 1825$ cm^{-1}, the growth lifetime is likely to be biased toward too small a value.[16] We therefore assume that the decay kinetics at $\tilde{\nu} = 1832$ cm^{-1} are consistent with the growth kinetics at $\tilde{\nu} = 1825$ cm^{-1}. From this, it follows that **A** is a precursor to **B**.

No difference was found between the experiments performed under argon and oxygen atmospheres.

The 1832 cm^{-1} transient cannot be due to the fluoroformyloxy radical, FC(O)O$^•$, which in an argon matrix has been reported to show a carbonyl frequency at $\tilde{\nu} = 1494.5$ cm^{-1}.[15] The low-wavenumber transition reflects the bond order of ca. 1.5 of each C−O bond in this molecule. The fluoroformyl radical FCO$^•$, on the other hand, has been reported to show a carbonyl frequency in an argon matrix at $\tilde{\nu}_{C=O} = 1855$ cm^{-1}.[9,10] At a standard DFT level of theory (B3LYP/6-31G*, frequency scaled by 0.9614), this value is nicely reproduced ($\tilde{\nu}_{C=O} = 1852$ cm^{-1} (calcd)). Including solvation by bulk acetonitrile (scipcm-B3LYP/6-31G*), the scaled calculated carbonyl frequency of FCO$^•$ is reduced to $\tilde{\nu} = 1832$ cm^{-1}, in perfect agreement with our experimental findings. The short-lived transient at $\tilde{\nu} = 1832$ cm^{-1} is therefore assigned to the fluoroformyl radical, FCO$^•$. Oxygen purging did not change the behavior of FCO$^•$, which is consistent with earlier predictions of a small activation enthalpy (PUMP4//UHF/6-31G*: $\Delta H^{\#} = 3.1$ kcal/mol) for the reaction leading to the fluoroformylperoxy radical.[17a] We have now recalculated this activation enthalpy at the UCCSD(T) level of theory[17b] and have found very similar values of $\Delta H^{\#} = 3.2$ kcal/mol (*E*) or 3.4 kcal/mol (*Z*), with reaction enthalpies of $\Delta H = -35.7$ kcal/mol (*E*) or -34.5 kcal/mol (*Z*). Given these data, we can conclude that unlike other acyl radicals,[2,3,18] **3** will not react with $^3O_2$ at the diffusion-controlled limit. Of importance, however, could be reactions of FCO$^•$ with the solvent, acetonitrile. Again, employing B3LYP/6-31G*, we calculated a number of possible reaction pathways for the FCO$^•$ plus acetonitrile reaction. The results are shown in Scheme 2.

The results show that all three reaction pathways, hydrogen abstraction, addition to C, and addition to N, are exothermic. The most favorable, in terms of both exothermicity and activation enthalpy, is addition to the nitrile carbon atom, yielding the *Z*-conformer of fluoroformyl-substituted iminyl radical **4**. The calculated vibrational spectrum of **4** includes an intense carbonyl stretch at $\tilde{\nu} = 1827$ cm^{-1}. The inclusion of bulk solvation by acetonitrile shifts this band to $\tilde{\nu} = 1812$ cm^{-1}. Considering the fact that our experimental resolution is 6 cm^{-1}, this still is in reasonable agreement with the position of the IR band of the secondary transient at $\tilde{\nu} = 1825$ cm^{-1}. Other possible secondary products, such as formyl fluoride **6** or the iminoyl radical **7**, are not in agreement with the experimental data. While **6** is known to be a stable molecule,[19] **7** is predicted to show two intense IR bands, a $\nu_{C=O}$ at $\tilde{\nu} = 1791$ cm^{-1} and a $\nu_{C=N}$ at $\tilde{\nu} = 1856$ cm^{-1}, which would be inconsistent with the experimental findings. A calculated activation enthalpy of 6.3 kcal/mol for addition to the nitrile carbon atom would translate into a lifetime of $\tau = 4$ μs (assuming log A = 10) for **3**, which is in qualitative agreement with the experimentally determined transient lifetime of $\tau = 3$ μs. The preference for reaction of FCO with the solvent in oxygen-saturated acetonitrile probably stems from the huge difference in concentrations, with $[CH_3CN] = [O_2] \times 2100$. A calculated activation enthalpy $\Delta H^{\#} = 3.2$ kcal/mol for reaction of FCO with $^3O_2$ translates into an estimated rate constant of $k = 3.4 \times 10^5$ s^{-1} at $T = 295$ K, if log A = 10. Taking into account that two-thirds of all FCO/$^3O_2$ encounter complexes will be of an unproductive quartet spin manifold, this figure is reduced to $k = 1.1 \times 10^5$ s^{-1}, which would not be competitive with addition to acetonitrile.

Experimental data and calculated IR modes are summarized in Table 1.

The results presented are remarkable in that acyl-functionalized iminyl radicals such as the iminyl radical derived from benzil monoxime, PhC(N$^•$)C(O)Ph, are known to fragment easily, yielding the acyl radical and the nitrile.[20] The reasons for the relative stability of **4** are unclear at present. The O−C cleavage pathway observed upon excitation of **2** clearly is not the only one that occurs. The formation of carbon dioxide gives unequivocal evidence for N−O cleavage. However, we have not been able to detect any of the intermediates that could also be formed in this reaction pathway. The fluoroformyloxy radical,

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[16] Because of the relatively few data points available, a biexponential fit of the data at $\tilde{\nu} = 1825$ cm^{-1}, including both the growth and the decay, was not possible.

[17] (a) Francisco, J. S.; Zhao, Y. *Chem. Phys. Lett.* **1988**, *153*, 296−302. (b) Energy minima: UCCSD(T)/cc-pVTZ. Transition states: UCCSD(T)/cc-pVTZ//UCCSD(T)/cc-pVDZ. The C−O bond distance in the TS for formation of *E*-FCOOO is calculated as $R = 2.14$ Å. The TS is calculated to be almost planar. (*E*) refers to *E*-fluoroformylperoxy or to its TS of formation, and (*Z*) refers to *Z*-fluoroformylperoxy or to its TS of formation.

[18] Brown, C. E.; Neville, A. G.; Rayner, D. M.; Ingold, K. U.; Lusztyk, J. *Aust. J. Chem.* **1995**, *48*, 363−379.

[19] Wong, M.; Johns, J. W. C.; McKellar, A. R. W. *J. Mol. Spectrosc.* **1982**, *94*, 79−94.

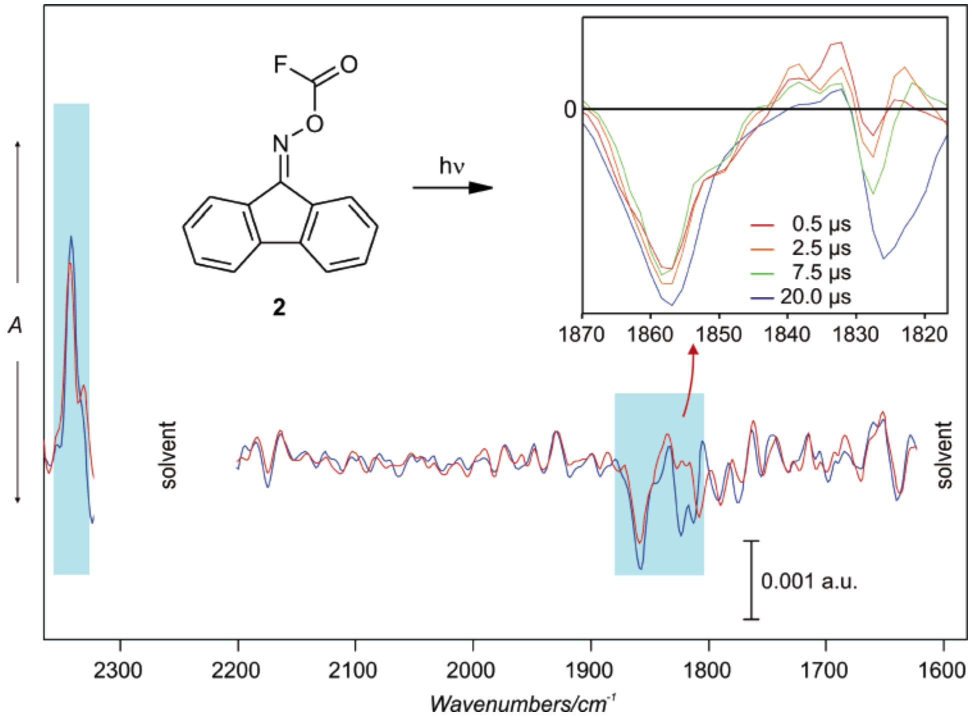


FIGURE 1. TRIR difference spectra (time resolution of 500 ns, spectral resolution of 6 cm^{-1}) following LFP (266 nm, 6 ns, $\sim$4 mJ/pulse) of fluoroformyl oxime **2** in acetonitrile under argon atmosphere. Bands appearing on irradiation are pointing upward; bands disappearing are pointing downward. Red: 500 ns after LFP. Blue: 20 μs after LFP. Important regions are highlighted in cyan. Inset: magnification of the 1810−1870 cm^{-1} region at four different times.

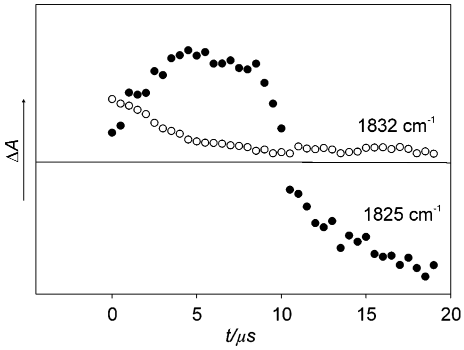
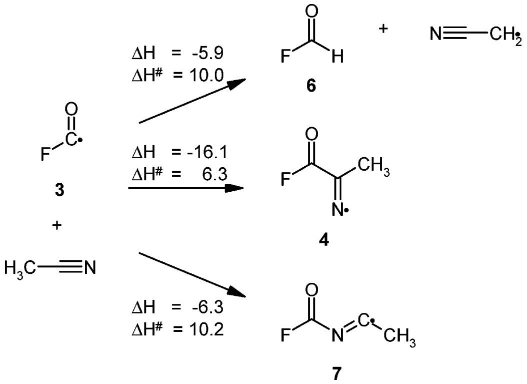


FIGURE 2. Transient kinetic traces, monitored after LFP (266 nm) of fluoroformyl oxime **2** in acetonitrile at $\tilde{\nu} = 1832$ (white dots) and 1825 (black dots) cm^{-1}.

SCHEME 2. Reaction Pathways for the Reaction of Fluoroformyl with Acetonitrile, as Calculated at the (B3LYP/6-31G* + ZPE) Level of Theory[a]



[a] All enthalpies are given in kcal/mol.

FC(O)O$^\bullet$, should have a barrier to decarboxylation that is high enough to allow for its detection.[11] Fluoroformic acid, FC(O)OH, which is a likely product formed by hydrogen abstraction of FC(O)O$^\bullet$ from the solvent, should also be readily detectable by TRIR spectroscopy.[21] It is conceivable that the 266 nm photons used for excitation contain sufficient energy to lead to rupture of both the N−O and C−F bonds. The very small signal intensities observed upon 355 nm excitation of **2** may indicate that photon energy indeed plays a role in the reaction. If this hypothesis is correct, 266 nm excitation of **2** should result in the formation of fluorine atoms, which is an intriguing proposition, even though their lifetime in acetonitrile will be exceedingly short.[22] As far as the photochemistry of the chlorooxalyl derivative **1** is concerned, our failure in detecting the chloroformyl radical ClCO$^\bullet$ likely is due to

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(20) (a) Groenenboom, C. J.; Hageman, H. J.; Oosterhoff, P.; Overeem, T.; Verbeek, J. *J. Photochem. Photobiol., A* **1997**, *107*, 261−269. (b) At the UB3LYP/6-31G* level of theory, the addition of PhCO to the nitrile C atom of benzonitrile, yielding PhC(O)C(N$^\bullet$)Ph, is calculated to be exothermic by 5.9 kcal/mol, with an activation enthalpy of 8.6 kcal/mol. The reaction is less favorable than the addition of FCO$^\bullet$ to acetonitrile but appears to be viable. Conversely, the fragmentation of PhC(O)C(N$^\bullet$)Ph, as observed by Groenenboom and co-workers, is predicted to be endothermic and thus has to be driven by the entropy term.

(21) Monomeric FCOOH has been calculated to show a fairly high activation enthalpy for decay into CO_2 and HF ($\Delta H^{\#} = 30.3$ kcal/mol, UMP2/6-311G** + ZPE). See: Francisco, J. S.; Ghoul, W. A. *Chem. Phys.* **1991**, *157*, 89−98. Hence, the very intense C=O band of FCOOH (calculated at $\tilde{\nu} = 1810$ cm^{-1}) should have been readily detectable in our experiments, and monomeric FCOOH in acetonitrile solution is unlikely to have a lifetime in the low microsecond range only. Furthermore, decay of FCOOH would have to be coupled to a secondary formation of carbon dioxide, which we do not observe.

TABLE 1. Lifetime, Experimental, and Calculated C═O[a] Stretching Vibrations of the Transient Species

	$\tilde{\nu}_{C=O}$ exptl [cm^{-1}]	τ exptl [μs]	$\tilde{\nu}_{C=O}$ calcd (gas phase) [cm^{-1}]	$\tilde{\nu}_{C=O}$ calcd (bulk CH_3CN) [cm^{-1}]
3	1832	3.3 ± 0.7	1852	1832
4	1825	5.0 ± 0.7	1827	1812
6			1843	1809
7			1810	1791
			1843 ($\nu_{C=N}$)	1856 ($\nu_{C=N}$)

[a] B3LYP/6-31G*, frequency scaled by 0.9614.

the known instability of this species toward dissociation into Cl$^{\bullet}$ and CO. The Cl−C(O)$^{\bullet}$ bond only has a BDE of ca. 5 kcal/mol.[8,23] Thus, it appears likely that, in analogy to the 266 nm photolysis of **2**, the 355 nm photon carries sufficient energy to cleave both the N−O and C−Cl bonds in **1**.[24]

Experimental Section

Synthesis of *O*-Fluorocarbonyl-9-fluorenone Oxime (2): 0.8 g (0.004 mol) of 9-fluorenone oxime was suspended in 80 mL of dry CCl_4. At a temperature of −7 °C, 25 mL of a 0.5 M solution of monofluorophosgene (COClF) in toluene (0.0125 mol) was added dropwise. The solution was allowed to warm gradually to ambient temperature. It was then stirred for an additional 18 h. The residual monofluorophosgene was removed from the solution by purging with argon. It was safely disposed of by bubbling the Ar stream containing the COClF through concentrated aqueous NaOH. The solution was filtered and evaporated to dryness. The light-yellow product was recrystallized from *n*-hexane (mp 124 °C (not corrected), yield 0.73 g (76% of theory)).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.02 (d, 1H), 7.73 (d, 1H), 7.47 (d, 1H), 7.45 (d, 1H), 7.38 (t, 1H), 7.34 (t, 1H), 7.21 (t, 1H), 7.18 (t, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 161.1 (C═O), 145.6 (C═N), 143.4, 142.8, 142.0, 134.0, 133.0, 131.3, 130.0, 129.4, 129.2, 124.16. 121.0, 120.9. ^{19}F NMR ($CDCl_3$, 235 MHz): δ = 52.76. IR (KBr): $\tilde{\nu}$ = 1857, 1637, 1610, 1596, 1453, 1321, 1196, 1172, 1042, 1016, 955, 885, 784, 758, 748, 730, 679, 645, 618 cm^{-1}. MS: *m*/*z* (%, assignment) = 241 (80, M$^+$), 178 (100, M$^+$ − CO_2F), 164 (10, M$^+$ − NCO_2F), 151 (35, M$^+$ − $CHNCO_2F$). HR-MS: 241.055300 calcd for $C_{14}H_8NO_2F$; 241.053907. Elemental analysis: found for $C_{14}H_8NO_2F$ C = 69.64%, H = 3.24%, N = 5.73%; calcd for $C_{14}H_8NO_2F$ C = 69.71%, H = 3.34%, N = 5.81%.

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Supporting Information Available: Experimental details, TRIR spectrum observed upon LFP of **1**, computational details, Cartesian coordinates of stationary points optimized. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) (a) Bucher, G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 10076−10079. (b) We cannot rule out the formation of *N*-fluoro-9-fluorenoneimine in a concerted process. However, N−F bond formation concerted with CO_2 extrusion would have to occur via a strained transition state involving a four-membered ring, which appears unlikely. The formation of FCOOO in a vibrationally hot state that rapidly decarboxylates appears more plausible.

(23) (a) Francisco, J. S.; Goldstein, A. N. *Chem. Phys.* **1988**, *128*, 367−372. (b) Walker, L. C.; Prophet, H. *Trans. Faraday Soc.* **1967**, *63*, 879−882.

(24) We note that we have not been able to detect free CO in our TRIR experiments with **1**. This is likely due to the fact that the intensity of ν_{as} of CO_2 is higher than the intensity of the CO band by a factor of ca. 8. The absorption of CO thus remains hidden in the experimental noise.