

IR spectroscopic characterization of intermediates in a gas-phase ionic reaction: The decarbonylation of Co^+ (acetophenone)

Robert C. Dunbar^{a,*}, David T. Moore^{b,1}, Jos Oomens^b

^a Chemistry Department, Case Western Reserve University, Cleveland, OH 44106, USA

^b FOM Institute for Plasma Physics “Rijnhuizen”, Edisonbaan 14, 3439MN Nieuwegein, The Netherlands

Received 31 October 2006; received in revised form 30 January 2007; accepted 7 February 2007

Available online 13 February 2007

Abstract

Decarbonylation of acetophenone is a facile process mediated by Co^+ complexation. Structures of two species on the gas-phase reaction path have been characterized by their infrared photodissociation spectroscopy, namely the Co^+ (acetophenone) complex itself, and the decarbonylated but still complexed product ion $\text{Co}^+(\text{C}_7\text{H}_8)$. Infrared spectra over the 500–1800 cm^{-1} frequency range were obtained by wavelength-dependent multiple-photon dissociation using the FELIX free electron laser and a Fourier-transform ion cyclotron resonance mass spectrometer. Structural characterizations were made by comparison with predicted spectra calculated by density functional theory (DFT) using the B3LYP functional. The initial complex Co^+ (acetophenone) was found to be intact, with little or no presence of rearrangement or bond-inserted structures. The spectrum indicates a mixture of O-bound and ring-bound isomers of this complex. The decarbonylated product ion was assigned to have the most stable structure, namely Co^+ (toluene), with no indication of the presence of possible bond-inserted isomers having a two-coordinate metal ion. A decarbonylation path involving metal ion insertion adjacent to the carbonyl group was suggested, and the corresponding bond-inserted complexes were computed to be energetically reasonable intermediate structures on the reaction path.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Decarbonylation reaction; IRMPD; IR spectroscopy; FT-ICR; Free electron laser

1. Introduction

Decarbonylation of aldehydes and ketones is a common process which can often be catalyzed by late transition metals. For instance, Rh (in Wilkinson’s catalyst) promotes selective decarbonylation of aldehydes [1,2] and ketones [3,4] in solution. Loss of carbonyl from energized gas-phase ketone complexes of Co^+ and Ni^+ has been studied many times as a low-energy decomposition pathway [5–10]. Some of the earliest gas-phase characterization of transition metal organometallic chemistry in the well controlled conditions of the FT-ICR ion trap was the study by Halle et al. [6] of the fragmentation chemistry of Co^+ /ketone complexes, in which the oxidative metal insertion into C–C bonds of the ketone was used as the basis for interpreting the observed fragmentation chemistry.

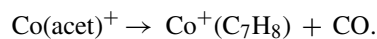
Although conclusions about the structures and interconversions of the various species along gas-phase organometallic reaction paths can be, and have been drawn and supported by many kinds of indirect evidence, the satisfactory spectroscopic verification of these structures has generally not been possible. New approaches to spectroscopy of complex gas-phase ions are available which greatly enlarge the possibilities for doing this [11–20]. In particular, IR spectroscopy over a wide spectral range made possible by a free-electron laser source in combination with capable mass spectrometers gives the opportunity to do IR-spectroscopic characterization of intermediates and products in metal-catalyzed gas-phase reaction sequences [11,12,19]. The spectroscopic richness of the acetophenone ligand makes it an especially attractive molecule as a basis for such a strategy, and the transition-metal catalyzed decarbonylation reaction provides a reaction path with sufficient interest and uncertainty to make it a good subject of study.

We have previously reported the spectroscopic characterization of *bis*-complexes resulting from attachment of several transition metal ions, including Co^+ , to acetophenone (acet) [11].

* Corresponding author. Tel.: +1 216 368 3712; fax: +1 216 368 3006.
E-mail address: rcd@po.cwru.edu (R.C. Dunbar).

¹ Present address: Chemistry Department, University of California Berkeley, Berkeley, CA 94720, USA.

In the cases of Ni⁺ and Cr⁺, a strong preference for binding the metal ion at the oxygen was found. However, the exceptional affinity of Co⁺ for π complexation to benzene rings resulted in a more complex situation for this ion, giving a mixture of O-bound and ring-bound Co(acet)₂⁺ complexes [11]. The strongly binding character of this metal ion is also displayed in its ability to catalyze dissociation reactions, as found in the present system with the abundant production of decarbonylated complexes Co(C₇H₈)⁺ and Co(C₇H₈)(acet)⁺. Due to the presence of multiple binding sites and the conformational flexibility of acetophenone, it is expected that such decarbonylations must take place on a potential energy surface of some complexity, involving several possible reaction pathways and product structures. It was the goal of the present study to gain insight into the catalytic activity of the Co⁺ ion in these decarbonylation processes, by direct spectroscopic characterization of the complex before and after decarbonylation, and by computational characterization of the intermediate structures along putative decarbonylation reaction pathways. The reaction of primary interest is



In the present work, as in our previous study [11], it was found that the simple attachment of a transition metal ion to the neutral molecule in our mass spectrometer did not result in a useful extent of production of the mono-complex M⁺(acet). This contrasts with the easy and efficient generation of the bis complexes M⁺(acet)₂ in the FT-ICR cell, apparently by ligand-transfer chemistry from other initially formed M⁺ complexes that were not characterized in these studies. As will be seen from the thermochemistry described below, the absence of the mono-complex can be understood from the fact that the directly formed Co⁺(acet) complex has ample internal energy to drive the decarbonylation reaction, so that an encounter of Co⁺ with a free acetophenone ligand results either in production of the Co⁺(acet-CO) fragment complex, or in redissociation of the metastable collision complex back to reactants. However, in the present study it proved possible to produce the Co⁺(acet) mono-complex by an alternative route, namely the mild collision-induced dissociation (CID) of the Co⁺(acet)₂ complex. It is this indirectly generated mono-complex that was spectroscopically characterized in the present study.

Two questions of metal-complex structures are of principal interest here. First: For the Co(acet)⁺ complex, the possibility exists that its formation by the somewhat energetic CID route that was used here might result in rearrangement to the more stable Co(toluene)(CO)⁺ complex, which should be spectroscopically distinguishable from Co(acet)⁺. Second: For the decarbonylated complex Co(C₇H₈)⁺ there are several possible product ion structures, and the IR spectrum should allow us to determine which of these are present.

2. Experimental

The general experimental procedure for obtaining infrared multiple photon dissociation (IRMPD) spectra of metal-molecule complexes in our Fourier transform ion-cyclotron resonance (FT-ICR) mass spectrometer has been described

in detail previously [11,14], and thus, only a brief summary is given here, along with a description of the new aspects of the experiment. Co⁺ ions were produced by laser ablation/ionization from a Co sputter target (GoodFellow, 99.98%), and introduced into the FTICR cell. There they were reacted with a pulse of acetophenone vapor, drawn from the volume above a liquid sample (Aldrich, 99%) from which dissolved gases had been removed using standard freeze/pump/thaw cycles. The resulting complexes were stored for several seconds to allow the complexes of interest to form and cool via spontaneous emission toward the ambient trap temperature (300 K).

The chemistry following reaction of Co⁺ with acetophenone in the ion-trapping cell resulted in strong peaks at m/z 299 [Co(acet)₂]⁺, m/z 271 [Co(acet)(C₇H₈)]⁺, and m/z 151 [Co⁺(C₇H₈)]⁺. No significant amount of the mono-complex ion [Co(acet)]⁺ at m/z 179 was observed except when this ion was specifically produced by CID of the m/z 299 ion in the ICR cell, as below. The bis-acetophenone complexes were fragmented using CID by sustained off-resonance irradiation (SORI) [21], to produce the desired Co(acet)⁺ complexes. The amplitude and duration of the SORI excitation were chosen to produce a useful amount of Co(acet)⁺, without driving it too far toward production of the decarbonylated mono complex at m/z = 151. An additional isolation time of 1 s was added to allow relaxation of any residual internal excitation from the SORI-CID process. Once produced, the parent Co(acet)⁺ complexes were isolated using a SWIFT pulse [22], and irradiated with tunable infrared light from the free-electron laser FELIX [23]. IRMPD spectra were generated by monitoring the total fragmentation yield as a function of the infrared frequency.

Structures, energies and harmonic infrared spectra were calculated by DFT/B3LYP using the Gaussian 03 package [24] with a basis consisting of 6–311 + g(d) on Co and 6–31 + g(d,p) on the other elements. The computed IR frequencies were scaled by a factor of 0.976, which was found to be the scaling factor giving the best fit to the neutral acetophenone IR spectrum at the same computational level. Since the position of the carbonyl stretching peak is important for assigning the spectra, it is important to note that, as observed in the previous study [11], the DFT calculation with this scaling factor systematically overestimates the carbonyl stretching frequency by $\sim 30 \text{ cm}^{-1}$ in the spectrum of the free acetophenone. For plotting in the figures, the calculated IR absorption spectra were convoluted with a Gaussian lineshape with a full width at half maximum of 30 cm^{-1} .

3. Results and discussion

3.1. Structure of the reactant mono-complex at m/z 179

The IRMPD spectrum of the mono-complex Co⁺(acet) (m/z 179) is shown in the top panel of Fig. 1. Possible structures for this complex are: (a) the intact acetophenone ligand is bound to Co⁺ either over the aromatic ring (**1**) or at the oxygen (**2**); (b) the metal ion has inserted by oxidative addition into one of the R–C bonds of RR'CO giving R–Co⁺–CO R' (**3** and **4**); (c) the

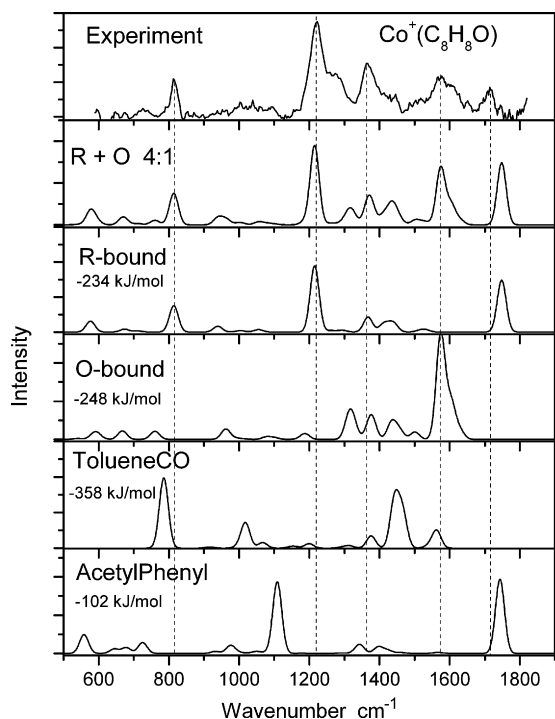
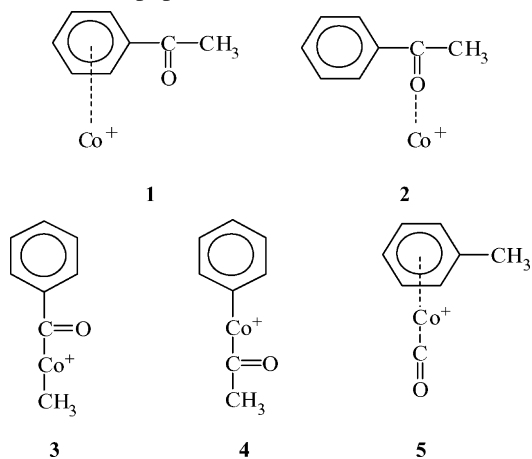


Fig. 1. IRMPD spectrum of the m/z 179 ion (top panel), along with DFT-computed spectra and energies of several possible isomers of the ion. Computed energies are given relative to the separated Co^+ /acetophenone pair.

potential energy surface has been traversed all the way to the most stable $\text{Co}^+(\text{CO})(\text{toluene})$ structure (5). We will show that the spectrum rules out both possibilities (b) and (c) as significant contributors to the population of these ions.



Calculated DFT spectra for these proposed structures are presented in the lower panels of Fig. 1. The calculated spectrum of $\text{Co}^+(\text{CO})(\text{toluene})$ (5) predicts a major peak (ring-methyl C–C stretch) at 1450 cm^{-1} , where little or no intensity is observed, and predicts the ring out-of-plane C–H umbrella mode to be at 790 cm^{-1} , which is not a good match to the observed peak at 810 cm^{-1} . Moreover, the predicted spectrum has no features matching the strong peaks observed at 1715 cm^{-1} , or 1215 cm^{-1} , and at best minor features that could match the peaks at 1370 cm^{-1} and 1470 cm^{-1} . So the match of the observed spectrum to this structure is poor, indicating that fraction of $\text{Co}^+(\text{CO})(\text{toluene})$ in the population is small at the very most.

Similarly, a significant amount of the bond-insertion structure $\text{Co}^+(\text{acetyl})(\text{phenyl})$ (4) is ruled out by the almost complete mismatch between the experimental spectrum and the predicted spectrum shown for this structure in the figure. A predicted spectrum for the other possible bond-insertion structure, $\text{Co}^+(\text{benzoyl})(\text{methyl})$, (3) is not shown, but it gives an even worse match to the observed spectrum than (4).

Based on the above comparisons, the parent $\text{Co}^+(\text{acet})$ complex must contain predominantly unreacted acetophenone ligand molecules. However, as seen from the predicted spectra in the figure, neither the R-bound (1) nor the O-bound (2) structure uniquely matches the experimental spectrum, and it is necessary to postulate a mixed population. The intense peak near 1600 cm^{-1} can only come from an O-bound structure (O-bound C=O stretch), while the experimental features at 1715 cm^{-1} (R-bound C=O stretch), 1210 cm^{-1} (ring-side-chain C–C stretch) and 810 cm^{-1} (out-of-plane ring hydrogen bending or umbrella mode) must be attributed to the R-bound structure [25]. As shown in the figure, a 4:1 superposition of 80% R-bound plus 20% O-bound yields a predicted spectrum for a mixed population that matches well with the observed spectrum [26]. The B3LYP calculation indicates that these two isomers are close in energy (O-bound more stable by 14 kJ/mol). In fact, a similar calculation using the MPW1PW91 functional, which has been considered to give a more accurate comparison between π -bound and π -bound transition-metal-ion complexes [14,15], reverses the predicted ordering, indicating 14 kJ/mol greater stability for the ring-bound isomer. Thus, these two structures have the same stability within computational uncertainty, and it is not surprising that a mixture of the two isomers would be formed. The fact that MPW1PW91 predicts higher stability of the ring-bound isomer, in agreement with the experimental indication, further supports the superiority of this functional in such calculations.

3.2. Structure of the decarbonylation product ion at m/z 151

In contrast to the parent complex, the decarbonylation product ion $\text{Co}^+(\text{C}_7\text{H}_8)$ is found to have rearranged completely to the most stable toluene-containing structure.

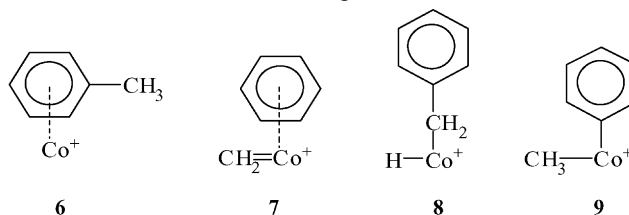


Fig. 2 shows the spectrum of the m/z 151 ion. It is an excellent match to the predicted spectrum for $\text{Co}^+(\text{toluene})$ (6). The major peaks near 800 cm^{-1} (ring umbrella), 1000 cm^{-1} and 1440 cm^{-1} are close in position and relative intensity to the predictions. The other reasonable possibilities are the $\text{Co}^+(\text{methylene})(\text{benzene})$ structure (7), and the bond-inserted structure $\text{Co}^+(\text{benzyl})(\text{H})$ (8). It is seen from the figure that predicted spectra of both of these are unacceptable, particularly in the $700\text{--}900\text{ cm}^{-1}$ region. The other bond-inserted possibility, $\text{Co}^+(\text{methyl})(\text{phenyl})$ (9), was calculated to be even less stable

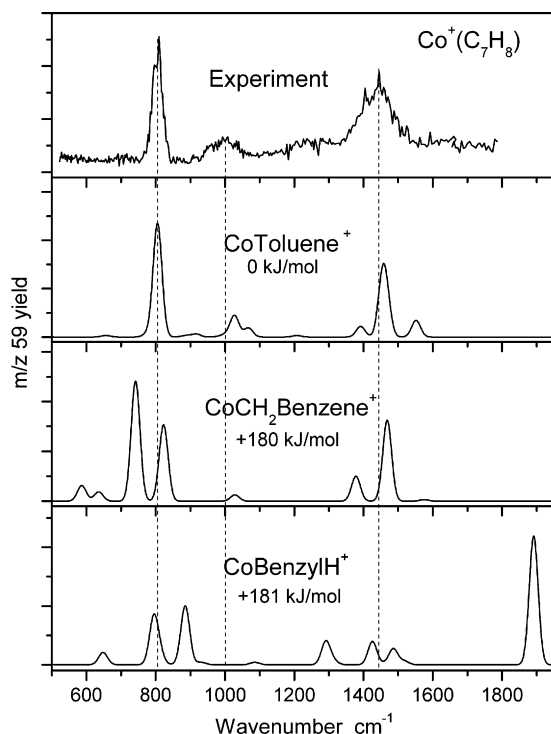


Fig. 2. IRMPD spectrum of the m/z 151 fragment ion resulting from reaction of Co^+ with acetophenone, along with computed spectra and energies of possible isomers. Energies are given relative to the most stable isomer, $\text{Co}^+(\text{toluene})$.

than $\text{Co}^+(\text{benzyl})(\text{H})$, and also to have a spectrum (not shown) very unlike the experimental one.

3.3. The decarbonylation reaction path

Fig. 3 shows the computed energies of key points on the potential energy surface of this system. It is not surprising that direct attachment of Co^+ to acetophenone does not yield stable mono-complex, since the initial attachment complex contains enough internal energy to access the postulated bond-inserted

intermediates with about 100 kJ/mol still available for overcoming any rearrangement barriers. (We can note that similar behavior was postulated for the $\text{Co}^+(\text{acetone})$ complex, based on kinetic energy release distribution (KERD) measurements [7].) Thus, the $\text{Co}^+(\text{acet})$ complex formed by direct attachment is definitely expected either to redissociate promptly back to reactants, or to traverse the reaction path to give m/z 151. In accord with these expectations, the present results clearly confirm that little or none of the parent complex population (m/z 179) finds its way to the much more stable $\text{Co}^+(\text{toluene})(\text{CO})$ complex (**5**) without the accompanying loss of the carbonyl to give m/z 151.

Also in accord with these expectations is the spectroscopic confirmation that none of the stable mono-complexes at m/z 179, accessed by the indirect synthetic route used here, have the bond-inserted structures (**3**) or (**4**), given that these two postulated intermediates resulting from oxidative bond-insertion rearrangements lie about 130 kJ/mol above either of the two parent complex structures (O-bound or ring-bound). Any m/z 179 ions having sufficient internal energy to access the bond-inserted isomeric structures would almost certainly continue on along the decarbonylation path leading to m/z 151.

Fig. 3 shows that the attachment of Co^+ to acetophenone provides enough internal energy to yield either of the indicated two-coordinate isomers of $\text{Co}^+(\text{C}_7\text{H}_8)$, namely $\text{Co}^+(\text{methylene})(\text{benzene})$ or $\text{Co}^+(\text{benzyl})(\text{H})$, accompanied by CO elimination. However, the spectral evidence in Fig. 2 clearly shows that these structures are not actually produced, indicating that, once the system has overcome the barrier to oxidative insertion, it always finds its way along the reductive coupling pathway yielding the most stable (toluene) complex.

4. Conclusions

The m/z 151 ion corresponding to decarbonylation of the Co^+ /acetophenone complex is shown spectroscopically to have the structure of the most stable isomer, $\text{Co}^+(\text{toluene})$. Various

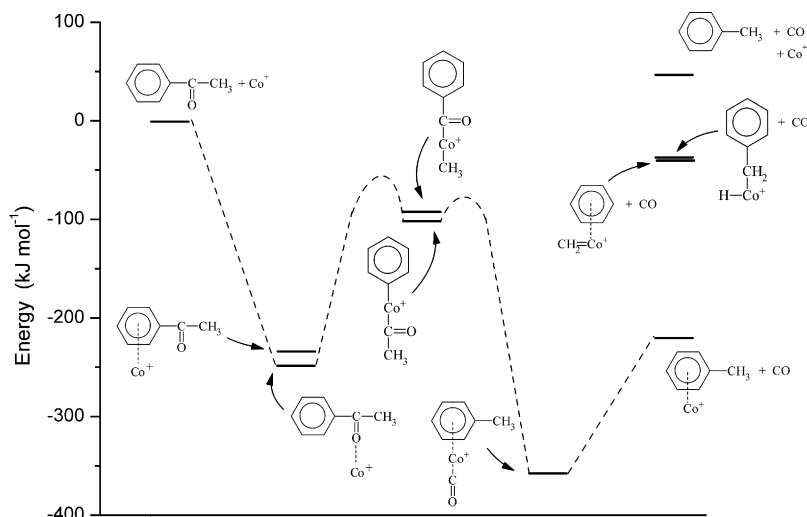


Fig. 3. DFT energies of various points on the Co^+ /acetophenone potential energy surface. A suggested schematic pathway is indicated (dashed line) for the decarbonylation reaction.

possible two-coordinate bond-inserted isomers of this ion are ruled out.

As expected from the reaction coordinate diagram in Fig. 3, attachment of Co^+ to acetophenone does not yield stable m/z 179 ions, because complexes formed in this way have more than sufficient internal energy to activate the decarbonylation to m/z 151. Stable m/z 179 ions synthesized by the alternative route of collision-induced dissociation of the *bis*-complex are found to have the structure of unrearranged $\text{Co}^+(\text{acet})$. The spectrum of $\text{Co}^+(\text{acet})$ clearly indicates a mixture of O-bound and ring-bound complexes of the intact acetophenone ligand.

Acknowledgements

This work is part of the research program of FOM, which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). The skilful assistance of the FELIX staff is gratefully acknowledged. RCD acknowledges the provision of travel funds by the National Science Foundation. Construction and shipping of the FT-ICR instrument was made possible with funding from the National High Field FT-ICR Facility (grant #CHE-9909502) at the National High Magnetic Field Laboratory, Tallahassee, Florida. We thank Professors John R. Eyler and Alan G. Marshall for their collaboration with the FT-ICR project.

References

- [1] J. Tsuji, K. Ohno, *Tetrahedron Lett.* (1967) 2173.
- [2] J. Tsuji, K. Ohno, *Tetrahedron Lett.* (1965) 3969.
- [3] E. Muller, A. Segnitz, *Ann. Der Chemie-Justus Liebig* (1973) 1583.
- [4] E. Muller, A. Segnitz, E. Langer, *Tetrahedron Lett.* (1969) 1129.
- [5] R.R. Corderman, J.L. Beauchamp, *J. Am. Chem. Soc.* 98 (1976) 5700.
- [6] L.F. Halle, W.E. Crowe, P.B. Armentrout, J.L. Beauchamp, *Organometallics* 3 (1984) 1694.
- [7] C.J. Carpenter, P.A.M. van Koppen, M.T. Bowers, *J. Am. Chem. Soc.* 117 (1995) 10976.
- [8] P.I. Surjasmita, B.S. Freiser, *J. Am. Soc. Mass Spectrom.* 4 (1993) 135.
- [9] S.S. Yi, E.L. Reichert, J.C. Weisshaar, *Int. J. Mass Spectrom.* 187 (1999) 837.
- [10] L.M. Zhao, R.R. Zhang, W.Y. Guo, S.J. Wu, X.Q. Lu, *Chem. Phys. Lett.* 414 (2005) 28.
- [11] R.C. Dunbar, D.T. Moore, J. Oomens, *J. Phys. Chem. A* 110 (2006) 8316.
- [12] G.S. Groenewold, A.K. Gianotto, K.C. Cossel, M.J. Van Stipdonk, D.T. Moore, N. Polfer, J. Oomens, W.A. de Jong, L. Visscher, *J. Am. Chem. Soc.* 128 (2006) 4802.
- [13] D.T. Moore, J. Oomens, J.R. Eyler, G. Meijer, G. von Helden, D.P. Ridge, *J. Am. Chem. Soc.* 126 (2004) 14726.
- [14] D.T. Moore, J. Oomens, J.R. Eyler, G. von Helden, G. Meijer, R.C. Dunbar, *J. Am. Chem. Soc.* 127 (2005) 7243.
- [15] J. Oomens, D.T. Moore, G. von Helden, G. Meijer, R.C. Dunbar, *J. Am. Chem. Soc.* 126 (2004) 724.
- [16] T.D. Jaeger, M.A. Duncan, *J. Phys. Chem. A* 109 (2005) 3311.
- [17] J. Velasquez, E.D. Pillai, P.D. Carnegie, M.A. Duncan, *J. Phys. Chem. A* 110 (2006) 2325.
- [18] T.D. Jaeger, D. van Heijnsbergen, S.J. Klippenstein, G. von Helden, G. Meijer, M.A. Duncan, *J. Am. Chem. Soc.* 126 (2004) 10981.
- [19] B.M. Reinhard, A. Lagutschenkov, J. Lemaire, P. Maitre, P. Boissel, G. Niedner-Schatteburg, *J. Phys. Chem. A* 108 (2004) 3350.
- [20] A. Simon, W. Jones, J.M. Ortega, P. Boissel, J. Lemaire, P. Maitre, *J. Am. Chem. Soc.* 126 (2004) 11666.
- [21] J.W. Gauthier, T.R. Trautman, D.B. Jacobson, *Anal. Chim. Acta* 246 (1991) 211.
- [22] A.G. Marshall, T.C.L. Wang, T.L. Ricca, *J. Am. Chem. Soc.* 107 (1985) 7893.
- [23] D. Oepts, A.F.G. van der Meer, P.W. van Amersfoort, *Infrared Phys. Technol.* 36 (1995) 297.
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, K.N.K.T. Vreven, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian03, Gaussian, Inc., Wallingford CT, 2004.
- [25] As in the dimer spectrum, the position of the carbonyl stretching mode is overestimated by $\sim 30 \text{ cm}^{-1}$. Similar discrepancies were also obtained with the MPW1PW91 functional (not shown). The consistent nature of this discrepancy suggests that it is a systematic error associated with the calculation, rather than a problem with the assigned structures.
- [26] The 4:1 ratio giving a good fit to the observed spectrum should not be considered as a quantitative result, since the peak intensities from harmonic frequency calculations are not quantitatively reliable predictors of IRMPD intensities. However, it is a clear indication that the ring-bound isomer is more abundant in the population.