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Radiative lifetime measurements of the CO and CD stretching modes in DCO^+

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Abstract

The radiative decays of vibrationally excited DCO^+ ions produced by dissociative ionization of CD_3CDO have been investigated using the monitor ion technique in a Fourier transform ion cyclotron resonance spectrometer. The radiative lifetimes of the ν_1 ($v = 1, 2$) and ν_3 ($v = 1$) stretching modes have been determined. For the CO stretching ν_3 the experimental lifetime (24 ± 2.5 ms) is in good agreement with the theoretical values calculated for DCO^+ and HCO^+. For the CD stretching ν_1 the experimental lifetimes (112 ± 22 ms) for $v = 2$ and (226 ± 45 ms) for $v = 1$ are about four times larger than the theoretical values. The disagreement between experiment and theory is possibly due to a strong coupling of ν_1 with a long lived state which has not been taken into account in the calculations. For the bending mode ν_2, only a lower limit of the very long lifetime could be evaluated. (Int J Mass Spectrom 185/186/187 (1999) 131–137) © 1999 Elsevier Science B.V.

Keywords: DCO^+; Radiative lifetimes; Internal energy content; Monitor ion technique

1. Introduction

Due to their astrophysical and chemical interest, the formyl ion HCO^+ and its high energy isomer HOC^+ have been subject to a large number of experimental and theoretical investigations. However, although the spectroscopy of the HCO^+ fundamental electronic state is well known, there was until recently very little information on the radiative lifetimes of its vibrational levels.

The results of the two most recent theoretical calculations [1,2] for the lifetimes of $v = 1$ levels of the three normal modes are in good agreement (Table 1). An experimental lifetime of 5.9 ms has been determined for $v = 1$ of mode ν_1 using direct laser absorption in a fast ion beam (DLASFIB) [3].

Finally, the so called "monitor ion technique" in a triple cell Fourier transform ion cyclotron resonance (FTICR) spectrometer has been used to measure the apparent lifetime of several levels in the bending mode [4]. These lifetimes have been shown to be in

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Dedicated to Professor M.T. Bowers on the occasion of his 60th birthday. It is a pleasure for two of us (R.M. and G.M.) to celebrate in this special issue more than 2 decades of fruitful interaction with Mike in the field of ICR mass spectrometry. Collaborating and/or competing, first on kinetic energy release measurements in charge transfer reactions at thermal energies, then on radiative lifetime measurements of long lived excited ions has been a stimulating challenge. Mutual attraction between Orsay and Santa Barbara induced several short and long visits from both sides over years . . . and even a marriage and three kids!

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Table 1
Theoretical radiative lifetimes (ms)

		ν_1	ν_2	ν_3
HCO^+	Sebald [2]	3.86	315	18.04
	Martin et al. [1]	3.7	334	21.1
DCO^+	Sebald [2]	50.8	13 000	18.1

good agreement with the theoretical radiative lifetimes assuming a Boltzmann population of the vibrational levels and an internal energy of 0.075 eV for HCO^+.

A second set of experimental lifetimes ranging from 9 to 33 ms has been also obtained and tentatively assigned to a combination of the stretching modes ν_1 and ν_3.

Because of the large isotope effect predicted for the ν_1 and ν_2 modes (see Table 1), similar experiments with DCO^+ were expected to provide interesting additional information. Indeed, on the time scale of our experimental technique, ν_2 should give a quasiconstant contribution to the decay curves, and ν_1 and ν_3 should be measurable separately.

In the present investigation, the monitor ion technique has been used to measure the radiative decay rates of excited DCO^+ ions as a function of their vibrational energy in order to determine the lifetimes of the vibrationally excited levels.

The objective of this study is to compare the experimental and theoretical lifetimes for DCO^+ and to check the predicted isotope effect for the C(D)H stretching mode.

2. Experimental conditions

The triple cell FTICR spectrometer used for lifetime measurements has been described several times and the monitor ion technique has been discussed in detail for HCO^+ [4,5]. The three cascaded ICR cells are separated by ion funnels to let the ions drift from cell to cell and maintain a pressure differential of around 250 between the low pressure central cell and the two other cells. It is important to recall that drifting the ions from one cell to the next one does not accelerate them since the drift velocity is small compared to the initial thermal velocity.

The DCO^+ ions are produced in the first cell (source) by dissociative ionization of CD_3CDO at typical pressures of 3.5×10^{-7} Torr using a 30 eV pulsed electron beam. The DCO^+ ions ($m/z = 30$) are mass selected by ejection of all the other ions, they are then drifted into the second cell where they are trapped for variable relaxation times. At the end of the relaxation time they are drifted into the third cell containing the monitor gas M, where they react at a constant pressure of around 1.5×10^{-6} Torr. The monitor reactions used in this study are deuteron transfer

$$DCO^+ + M \rightarrow MD^+ + CO$$

where the monitor gas M has a lower deuteron affinity than CO. The reaction is energetically allowed only for DCO^+ ions whose internal energy is higher than the reaction endothermicity. By using different monitor gases, the internal energy content of excited DCO^+ can be probed and its time evolution measured by varying the relaxation time.

After a constant reaction time (30 ms) the monitor MD^+ and the unreacted DCO^+ ions are drifted back into the central cell for detection by FTICR. Finally all the ions are ejected by a detrapping pulse. This sequence is repeated and the transient ICR signals accumulated for signal averaging until the signal/noise ratio is sufficient. Due to an efficient differential pumping, the pressure in the central cell, used as a relaxation cell and as a detection cell, is very low. The main components of the background gas are 1.4×10^{-9} Torr of CD_3CDO leaking from the source, 6.0×10^{-9} Torr of monitor gas leaking from the reaction cell and around 5×10^{-9} Torr of H_2O desorbing from the walls.

3. Data treatment

As discussed in detail for HCO^+ [4], the decay of the monitor ion signal MH^+ as a function of the relaxation time is due exclusively to the decay of the excited HCO^{+*} ions in the relaxation cell.

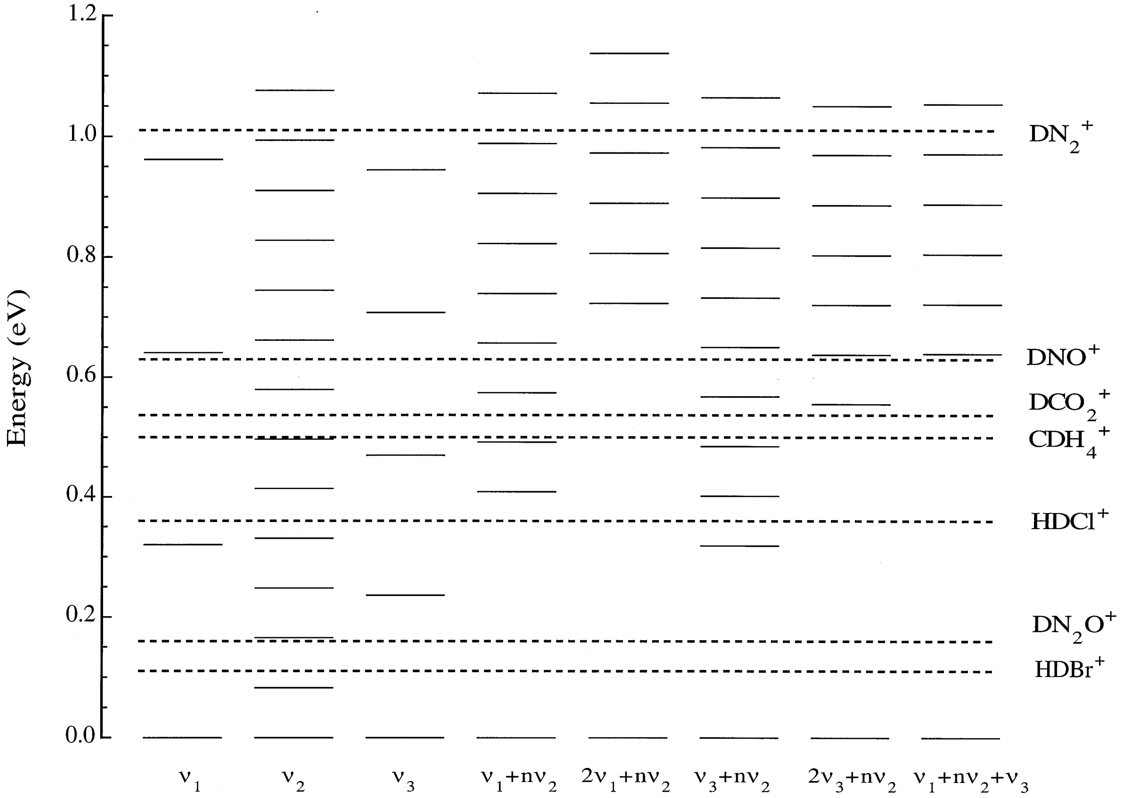

Fig. 1. Vibrational energy levels of DCO^+ ground electronic state calculated with the theoretical values of Puzzarini et al. [8] without correction for anharmonicity. The broken lines correspond to the threshold energies for the different monitor reactions.

It was also shown that the ratio $R = [MH^+]_3/([MH^+]_3 + [HCO^+]_3)$ measured at the end of the reaction time is proportional to the amount of excited $HCO^{+}*$ ions, leaving the relaxation cell with an internal energy large enough to react with the monitor molecules.

Therefore, R is a sum of exponential decays corresponding to the apparent decay rates of the vibrational levels of $HCO^{+}*$ located above the threshold energy of the monitor reaction. The level located just below may also react if the small endothermicity is compensated by the high energy tail of the kinetic energy distribution of the ions.

The experimental results for DCO^+ ions have been treated in the same way as for HCO^+. For each monitor the ratio $R = [MD^+]/([MD^+] + [DCO^+])$ as a function of the relaxation time was fitted to a sum of exponential decays. These experimental decay rates were then corrected for collisional quenching of $DCO^{+}*$ with the monitor gas in the relaxation cell.

4. Energetics of the monitor reactions

4.1. The vibrational energy diagram of DCO^+

Experimental values are available for the vibrational frequencies of the two normal modes: $\nu_1 = 2584.56\ \text{cm}^{-1}$ [6] and $\nu_3 = 1904.06\ \text{cm}^{-1}$ [7]. The more recent theoretical calculations [8] are in good agreement with the experimental values and with the values calculated by P. Sebald in P. Botschwina's group [2].

Fig. 1 shows a vibrational energy diagram constructed with the theoretical values of Puzzarini et al. [8]: $\nu_1 = 2585.9\ \text{cm}^{-1}$, $\nu_2 = 667.8\ \text{cm}^{-1}$ and $\nu_3 = 1903.97\ \text{cm}^{-1}$, without correction for anharmonicity. The ionization energy of DCO is 8.56 eV [9] and the high energy isomer DOC^+ is supposed to be 1.63 eV above DCO^+.

4.2. The monitor reactions

The monitor reactions used for DCO^+ are deuteron transfer and the monitor molecules are the same as for HCO^+ (i.e. HBr, N_2O, HCl, CH_4, CO_2, NO and N_2) but because of the difference in the vibrational frequencies between HCO^+ and DCO^+, they do not probe the same vibrational levels.

Moreover, due to the difference of the zero point energies, deuteron and proton affinities are different. The endothermicity of deuteron transfer reactions may be calculated for CO_2, N_2O and N_2 using the known vibrational frequencies: for CO_2 and N_2O deuteron transfer is less endothermic than proton transfer by 11 meV and 18 meV, respectively, and for N_2 it is more endothermic by 18 meV. No information is available for the other monitors but the difference of the endothermicities is probably of the same order of magnitude (±20 meV) which is comparable to the uncertainties on the proton affinities.

Therefore the threshold energies of deuteron transfer reactions to the different monitor molecules are supposed to be the same as proton transfer threshold energies. The broken lines in Fig. 1 correspond to the threshold energies derived from the two most recent experimental proton affinities determined by Adams et al. [10] and Szulejko and McMahon [11] which agree within 10–20 meV.

5. Results and discussion

5.1. Experimental decay curves

5.1.1. N_2 as monitor

$^{15}N_2$ had to be used instead of $^{14}N_2$ to separate the monitor ion $^{15}N_2D^+$ ($m/z = 32$) from the reactant ion DCO^+ ($m/z = 30$).

The signal at $m/z = 32$ was very small, indicating that the amount of the high energy isomer DOC^+ or of vibrational states of DCO^+ above 1 eV is very small.

5.1.2. HBr, N_2O, HCl, CH_4, CO_2, and NO as monitors

Because the monitor reaction with HBr has a very small endothermicity (0.1 eV), a large fraction of ground state DCO^+ may react and their contribution to the monitor ion signal makes the analysis of the experimental data difficult.

For all the other monitors the decay curves could be fitted to a sum of three exponentials, corresponding to three lifetimes, a short one τ_s, a long one τ_l and a very long one τ_{vl}. Fig. 2 shows a typical decay curve for DN_2O^+ monitor ions normalized to the sum ($[DCO^+] + [DN_2O^+]$).

An estimate of the collisional quenching rate of $DCO^{+}*$ with the monitor gas in the relaxation cell has been calculated for each monitor using the pressures measured in the reaction cell reduced by a factor of 250 and the corresponding capture rate constants evaluated by the formula of Su and Chesnavich [12]. This gives an upper limit of the quenching rate since collisional quenching may not occur at each collision. The radiative lifetimes deduced from the equation: $1/\tau_{\text{rad}} = 1/\tau_{\text{app}} - k[M]$ are reported in Table 2 for τ_s and τ_l. They differ from the measured lifetimes by less than 1% for τ_s and 5% for τ_l.

For the very long lifetimes τ_{vl} the quenching rates being of the same order of magnitude as the experimental decay rates, the radiative lifetimes cannot be determined. The experimental results only indicate that high levels of the corresponding mode are populated.

5.2. Assignment of the experimental radiative lifetimes

The shorter lifetimes τ_s are the same, within the experimental uncertainties, for all the monitor gases and their mean value $\tau_s = 24 \pm 2.5$ ms, is close to the theoretical lifetime of ν_3 ($v = 1$). As this level is just above the threshold for deuteron transfer with

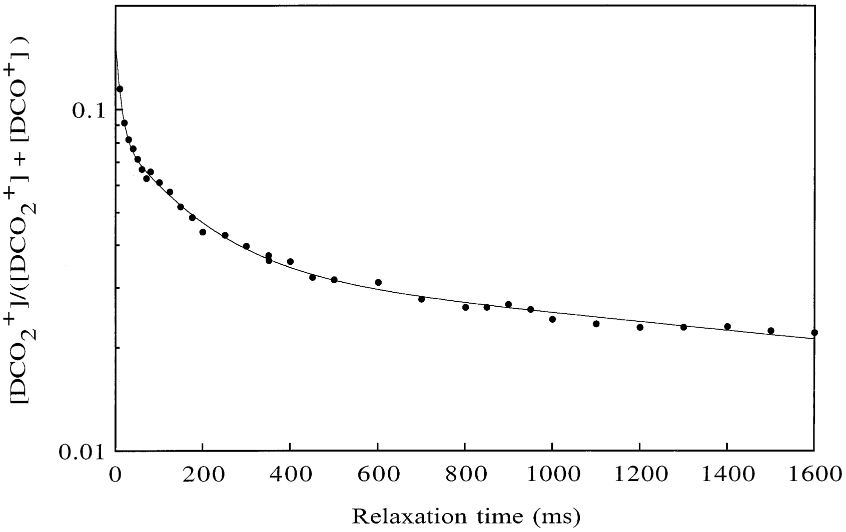

Fig. 2. Decay curve of the $[DCO_2^+]$ monitor ion normalized to the sum ($[DCO_2^+] + [DCO^+]$) as a function of relaxation time. Fitting a sum of three exponentials to the experimental data gives $\tau_s = 21.1$ ms, $\tau_l = 180$ ms and $\tau_{vl} \geq 3000$ ms.

N_2O, the short lifetime observed with this monitor can be assigned to level (0,0,1) (Table 3).

If higher levels of ν_3 were populated HCl should probe ν_3 ($v \geq 2$) and CH_4, CO_2 and NO should probe ν_3 ($v \geq 3$). Since in the harmonic approximation the lifetimes within a given mode varies like $1/v$ the lifetime measured with HCl should be smaller than with N_2O and even smaller with CH_4, CO_2 and NO. As the lifetimes are the same for all the monitors we conclude that the population of levels $v > 1$ is negligible.

As shown on Fig. 1 the compound mode levels $(0,n,1)$ can also react with the different monitors. The decay rate of these levels is the sum of the ν_2 ($v = n$) and ν_3 ($v = 1$) decay rates: $1/\tau_{0,n,1} = 1/\tau_{0,n,0} + 1/\tau_{0,0,1}$. However since the lifetimes of ν_2 ($v = n$) are predicted to be very long (13 000 ms for $v = 1$ to 1625 ms for $v = 8$) compared to ν_3 ($v = 1$) (20 ms), the lifetimes of levels $(0,n,1)$ must be very close to that of ν_3 ($v = 1$).

Table 2
Experimental radiative lifetimes (ms) and collision rates (s^{-1}) of DCO^{+*}. For each monitor, three lifetimes have been obtained by fitting the experimental decay curves to the sum of three exponentials: A short lifetime τ_s, a long one τ_l, and a very long one τ_{vl}

Monitors	τ_s	τ_l	τ_{vl}	Collision rate
NO	26.1	112	≥3000	$1.3\ 10^{-4}$
CO_2	21.1	180	≥3000	$1.4\ 10^{-4}$
CH_4	24.2	183	≥3500	$2.2\ 10^{-4}$
HCl	26.7	223	≥5000	$2.8\ 10^{-4}$
N_2O	23.1	283	≥6000	$1.7\ 10^{-4}$

This can explain the quite unexpected constant value of τ_s with the different monitors even if high levels of the bending mode ν_2 are populated as shown below.

The long lifetime τ_l exhibits a quite different behavior: It decreases as the threshold energy for the monitor reaction increases indicating that the C–D stretching mode is excited at least up to $v = 2$.

Fig. 1 shows that N_2O can react with levels ν_1 ($v \geq 1$) and also with the compound mode levels $(1,n,0)$. But for the same reason as for $(0,n,1)$ the lifetimes of these levels are very close to the lifetime of ν_1 ($v = 1$).

HCl can react with levels ($1,n \geq 1,0$) and ($2, n \geq 0,0$), and can also react slowly with level (1,0,0) since the reaction is slightly endothermic. The decay rate of $HDCl^+$ will therefore be a combination of (1,0,0) and (2,0,0) and the apparent lifetime, intermediate be-

Table 3
Comparison of experimental and theoretical lifetimes (ms)

	DCO^+		HCO^+		Isotopic effect	
	τ_{meas}	τ_{th}	τ_{meas}	τ_{th}	Measured	Theoretical
0,0,1	24 ± 2.5[a]	18.1[b]	?	21.1[e]	?	1
1,0,0	226 ± 45[a]	50.8[b]	5.9[c]	3.7[e]	38	13
0,1,0	≥6000[a]	13 000[b]	285–395[d]	334[e]	?	41

[a] Present work.
[b] Sebald [2].
[c] Keim et al. [3].
[d] Mauclaire et al. [4].
[e] Martin et al. [1].

tween the lifetimes of $v = 1$ and $v = 2$, depends on their relative populations.

CH_4 can react with levels $(1,n \geq 2,0)$ and $(2,n \geq 0,0)$, therefore the decay rate of DCH_4^+ will also be a combination of (1,0,0) and (2,0,0), but the contribution of (1,0,0) being smaller than for HCl, the apparent lifetime must be shorter.

CO_2 that can react with levels $(1,n \geq 3,0)$ and $(2,n \geq 0,0)$ will give an even shorter lifetime than CH_4.

Finally, NO that can react with DCO^+ $(1,n \geq 4,0)$ and $(2,n \geq 0,0)$ will probably give a lifetime very close to ν_1 $(v = 2)$.

So, the variation of the lifetime τ_l measured with the different monitors indicates that the radiative lifetime of the ν_1 $(v = 2)$ level is close to 112 ± 22 ms) and the overall lifetime of level ν_1 $(v \geq 1)$ close to 283 ± 55 ms.

The population of ν_1 $(v = 3)$ must be negligible since we observed almost no reaction with N_2.

The harmonic approximation would give for ν_1 $(v = 1)$ a lifetime twice as large as for ν_1 $(v = 2)$, i.e. 224 ms. The difference with the overall lifetime measured for $v \geq 1$ may be due to radiative cascade from the upper levels. As shown for CO^+ radiative cascade can lengthen appreciably the experimental lifetimes if high vibrational levels are populated [13]. In DCO^+ this effect may be large for ν_2 since high levels are populated, but not for ν_1 populated only up to $v = 2$. A lengthening of 20% seems reasonable, which gives a lifetime of 226 ms for ν_1 $(v = 1)$. The very long lifetimes observed with all the monitors (see Table 2) correspond certainly to the bending modes ν_2. Because they are observed with NO as monitor, levels up to $v = 8$ are probably populated.

6. Conclusions

By using the monitor ion technique in a triple cell FTICR spectrometer we have determined a radiative lifetime of 24 ± 2.5 ms for the CO stretching mode ν_3 $(v = 1)$, of DCO^+, in reasonable agreement with the theoretical value (18.1 ms).

The radiative lifetimes determined for the two first levels of the CD stretching mode ν_1, 112 ± 22 ms for $v = 2$ and 226 ± 45 ms for $v = 1$, are much longer than the theoretical values. Excitation of the bending mode up to level $v = 8$ is observed but the radiative lifetimes are too long to be determined in our experimental conditions.

All the experimental results can be accounted for in the framework of an excitation of high levels of the bending mode ν_2 (up to $v = 8$) as observed with HCO^+ [4], an excitation of the C–D stretching mode ν_1 up to $v = 2$ and excitation of the C–O stretching mode ν_3 only to $v = 1$. This seems reasonable in view of the geometry change between the parent molecule CD_3CDO and the fragment ion DCO^+. There is indeed a large variation of the DCO angle (120°–180°), a small increase of the D–C bond length and a still smaller change of the C–O bond length.

However, if this simple model can explain the variation of the experimental lifetimes with the internal energy of DCO^+, it does not explain why the experimental lifetime of ν_1 ($v = 1$) is four times larger than the theoretical lifetime giving an experimental isotope effect of 38 instead of the theoretical value of 13. This is in contrast with the reasonable agreement between the experimental and theoretical isotope effects obtained for the lifetimes of the stretching mode in $H(D)Br^+$ [14]: 5.3 and 4.1, and of the bending mode in $H_2(D_2)O^+$ [5]: 3.7 and 4.6.

A possible explanation for a radiative lifetime much longer than calculated could be a strong coupling with a long lived state. The effect of coupling between rovibronic states of DCO^+ has been discussed by Hirota and Endo [15] who proposed a strong anharmonic interaction between the $(1, 0^0, 0)$ and $(0,4^0, 0)$ states. In a recent theoretical investigation, Puzzarini et al. [8] do not confirm this interpretation and support instead the suggestion by Sebald and Botschwina [16] that the coupling occurs between the $(1, 0^0, 0)$ and the $(0, 1^1, 1)$ states. To our knowledge, no calculation of the possible effect of such a coupling on the radiative lifetimes is available to date.

Acknowledgements

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