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Matrix reactions of silver atoms with ozone molecules

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Our interest in electrode discharge environments recently led us to a matrix study of the various reactions of copper atoms with ozone.¹ As an extension of that work we have undertaken a similar study of the reactions between atomic silver and ozone. The results of that study are reported herein. The experimental parameters used in the present investigation have been previously detailed.² Silver atoms were thermally evaporated and condensed onto a 10K CsI window along with various Ar : O₃ samples. The gaseous Ar : O₃ samples were deposited at 3–4 mmole per hour for 4–6 h. Following deposition, infrared spectra were recorded on a Beckman IR-12 spectrophotometer in the 200–4000 cm⁻¹ spectral region.



WAVENUMBER (cm⁻¹)

FIG. 1. Infrared spectra in the 460-500 and 740-800 cm⁻¹ regions observed following codeposition of silver atoms with (top) $Ar/{}^{16}O_3 = 200/1$, (middle) $Ar/{}^{18}O_3 = 200/1$, and (bottom) $Ar/{}^{16,18}O_3 = 125/1$.

The reaction of silver atoms with an $Ar/{^{16}O_3} = 200/1$ sample produced a new infrared absorption at 499.2 cm⁻¹ as well as two new intense features at 791.8 and 798.3 cm⁻¹. When a similar experiment was performed using an ozone sample enriched to 99% with oxygen-18, these new bands were found at 474.5, 747.5, and 754.2 cm^{-1} . Silver atoms were also reacted with an argon-diluted ozone sample that was 50% enriched with oxygen-18. In this latter experiment two bands were produced at 474.5 and 499.2 cm⁻¹ with no intermediate features. The 745-800 cm⁻¹ region, on the other hand, contained at least ten well-resolved absorptions whose extreme members corresponded to bands observed in the pure isotopic experiments. These spectra are shown in Fig. 1. Accurate frequency measurements for all new bands are given in Table I.

The oxygen isotopic splitting pattern observed for the 499.2 cm^{-1} feature is indicative of a molecule with a single oxygen atom. The observed 24.7 cm⁻¹ oxygen-18 isotopic shift is in excellent agreement with that calculated for a harmonic diatomic Ag-O oscillator, 24.8 cm^{-1} . On this basis, the 499.2 cm^{-1} absorption is attributed to the AgO molecule. The frequency shift for the naturally occurring silver isotopes (0.6 cm⁻¹) was beyond our resolution capability. Support for the AgO assignment is obtained from gas phase emission results^{3, 4} which place the AgO fundamental frequency (ω_e $-2\omega_e \chi_e$) at 485 cm⁻¹. The 2.8% gas-to-matrix (Ar) blue shift is unusual, but not unprecedented. For example, MgO has been found to have a 6.8% gas-to-matrix (N_2) blue shift.⁵ On the other hand, the infrared spectrum of CuO¹ has recently been observed in ma-

TABLE I. Frequencies (cm⁻¹) and assignments of new infrared absorptions produced by codeposition of silver atoms with isotopic ozone samples diluted in argon.

Ag + ¹⁶ O ₃	Ag + ¹⁸ O ₃	Ag + ^{16,18} O ₃		Assignment
499, 2 791, 8	474.5 747.5 754.2	499.2 474.5 747.6 754.0 758.0 764.5 768.5 774.0° 778.5° 781.9 789.0	Ag Ag Ag Ag Ag Ag Ag Ag Ag Ag Ag	$ \begin{array}{c} 16\\ 18\\ 0\\ 18\\ 0\\ 3\\ 0\\ 18\\ 0\\ 18\\ 0\\ 18\\ 0\\ 16\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$
798.3		198.3	Ag	O_3

^{a, b}Site-split components of each isotopic species. ^cFrequencies used for O-O-O bond angle calculations. trices for the first time and found to have a very small (<0.2%) gas-to-matrix (Ar) frequency shift. The latter comparison implies that the gas phase emissions of AgO may not terminate in the ground state; however, further work is needed to confirm this supposition.

The new product bands in the 750-800 cm⁻¹ region are characteristic of the ozonide ion and accordingly are assigned to the AgO₃ molecule. The isotopic spectra, although complicated by a site-splitting effect, are consistent with a molecule containing two equivalent oxygen atoms and a third inequivalent oxygen atom. Furthermore, the frequency and total oxygen-18 isotopic shift are in accord with several other metal ozonide species in matrices.^{1,5-8} Bond angle calculations produce a value of $103^{\circ} \pm 4^{\circ}$ for the O-O-O angle in AgO₃ agreeing with those previously calculated for other metal ozonides.^{1,5-8}

McIntosh and $Ozin^9$ have reported argon matrix reactions between silver atoms and O_2 in which AgO₂ and AgO₄ species were identified. We did several experiments by codepositing silver atoms with argon-diluted O_2 samples and find general agreement with their results. In particular, no bands attributable to the AgO absorptions were observed in these experiments, proving that the 499.2 cm⁻¹ band is a genuine silver atom- O_3 reaction product. AgO is not expected to be produced by reaction of silver atoms with O_2 since the AgO bond strength is only about 50 kcal/mole.¹⁰

The present results support a branching mechanism in which silver atoms can either abstract an oxygen atom from ozone to form AgO or transfer an electron and form $Ag^*O_3^*$. This result is identical to the result for copper atom reactions¹ with ozone described in previous work from this laboratory, as well as in matrix reactions of other metal atoms with ozone reported by Andrews and co-workers.⁵⁻⁸

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Millimeter and submillimeter spectra of HCO⁺ and DCO⁺

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The J=0-1 transitions of six different isotopic forms of the HCO⁺ molecular ion have been studied by Woods and collaborators.¹ We report here the extension of this work into the shorter millimeter and submillimeter region and the measurement of these spectra through J=4-5 for HCO⁺ and J=5-6 for DCO⁺. These measurements, combined with our study of ion drift velocities discussed below, provide accurate rotational constants and rest frequencies for these astrophysically important species. The ions were produced in a Pyrex glow discharge cell 1 m in length and 10 cm in diameter which was cooled to liquid N₂ temperature. The total pressure was optimized at ~40 mTorr with equimolar amounts of CO and H₂(D₂), but discharge currents of 100-500 mA reduced the pressure on the pump end of the cell to ~20 mTorr, presumably by production of condensable species

TABLE I.	Observed	rotational	transitions	of HCO*	and DCO ⁺	(MHz).
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Transition $J'' \rightarrow J'$	HCO*		DCO ⁺		
	Observed	ObsCalc.	Observed	ObsCalc.	
<u>1→2</u>	178 375. 065(50) ^a	0.022	144 077, 319(50) ^a	0.003	
2→3	267 557.619(10) ^{a, b}	- 0,001	216 112, 604(50) ²	-0.018	
$3 \rightarrow 4$	356 734, 288(50)	0.022	288 143. 911(50)ª	0.006	
4-+5	445 902, 996(50)	-0.005	360 169, 881(100) ^a	0.056	
5→ 6	• • •	•••	432 189, 033(50)	-0.008	

^aAlso detected by Bogey, Demuynck, and Destombes (Ref. 3).

^bHuggins et al. (Ref. 4) have obtained an astronomical frequency of 267 557. 20(46) MHz.

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