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COMMUNICATIONS

State-resolved two-photon laser induced fluorescence detection of BrO

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In the present work we report state-resolved detection of BrO($X\ ^2\Pi$) radicals generated in reactive collision processes using two-photon excitation with subsequent monitoring of the vacuum-ultraviolet fluorescence. BrO($X\ ^2\Pi$) product excitation spectra extending in the spectral range between 348 and 363 nm were obtained from both the reaction O(^1D)+CF$_3$Br and Br($^2P_{3/2}$)+O$_3$. The spectra indicate the existence of a hitherto unobserved high-lying radiative C state at an energy of around 56 000 cm^{-1}. *© 1998 American Institute of Physics.* [S0021-9606(98)02430-1]

In the present work we report new state-resolved detection of BrO($X\ ^2\Pi$) radicals generated in reactive collision processes using two-photon excitation with subsequent monitoring of the vacuum-ultraviolet fluorescence emanating from a hitherto unobserved BrO electronic state at an energy near to 56 000 cm^{-1}. Catalytic reaction cycles involving ClO and BrO radicals are supposed to be responsible for about 30 percent of the halogen-controlled loss of stratospheric ozone over Antarctica.[1] This importance of halogen monoxide free radicals for the atmosphere has motivated numerous studies addressing ClO, BrO, and IO.[2–6] In most investigations ClO and BrO radicals are observed by absorption using their well-known $A\ ^2\Pi - X\ ^2\Pi$ bands. In evaluating the gas-phase dynamics and mechanistics, however, detection methods which are more sensitive and state resolved in nature are required. Proven methods in meeting these requirements are resonance enhanced multiphoton ionization (REMPI)[7,8] as well as laser induced fluorescence (LIF) detection. LIF detection using the $C\ ^2\Sigma$ Rydberg state has in recent times successfully been employed in analyzing nascent state-resolved ClO($X\ ^2\Pi$) radicals formed in photodissociations and reactions.[9–11] However, this sensitive detection technique has to our knowledge never been applied to the observation of BrO($X\ ^2\Pi$) radicals. In this study, we report state-resolved two-photon laser induced fluorescence detection of BrO($X\ ^2\Pi$) radicals. BrO product excitation spectra extending in the spectral range between 348 and 363 nm were obtained from the reactions

$$\mathrm{O}(^1D)+\mathrm{CF_3Br}\rightarrow \mathrm{BrO}(X\ ^2\Pi)+\mathrm{CF_3}$$
$$\Delta H = -161.9\ \ \mathrm{kJ/mol.} \tag{1}$$

and

$$\mathrm{Br}(^2P_{3/2})+\mathrm{O_3}\rightarrow \mathrm{BrO}(X\ ^2\Pi)+\mathrm{O_2}$$
$$\Delta H = -129.5\ \ \mathrm{kJ/mol.} \tag{2}$$

O(^1D) reactants were generated by photolysis of ozone at a wavelength of 308 nm delivered by a XeCl excimer laser (Lambda Physik LPX100, 200 mJ/pulse). Ozone was synthesized in a silent discharge of molecular oxygen.[12] The BrO detection wavelength in the range of 348–363 nm was delivered by a tunable dye laser (Radiant Dyes DL-midi) pumped by a XeCl excimer laser (Radiant Dyes RD-EXC-200). The pulse duration was 15 ns and the dye laser output (dye RDC 360-neu) was 8–10 mJ/pulse at a bandwidth of 0.4 cm^{-1}. The two laser beams counterpropagated through the reaction chamber. The photolysis and detection laser beams were focused by 300 and 250 mm quartz lenses, respectively. The time delay between the pulses of the photolysis and the detection laser was varied between 0.2 and 3.5 microseconds. A solar-blind photomultiplier tube (Thorn EMI 9403B), which was not sensitive to the used excitation wavelength, was mounted perpendicular to the laser beams. In the reaction O(^1D)+CF$_3$Br a mixture of O$_3$–CF$_3$Br was employed, whereas the precursors Br$_2$ and O$_3$ in the reaction (2) were added separately to the reaction chamber. The production of Br($^2P_{3/2}$) atoms was achieved by irradiating gaseous Br$_2$ at 532 nm using the frequency doubled output of a Nd:YAG laser (Quanta Ray DCR1A-YAG, 100 mJ/pulse). Experiments were carried out under flow conditions sufficiently fast to prevent accumulation of primary and secondary reaction products.

The BrO two-photon LIF spectrum obtained from reaction (1) is represented in Fig. 1. The observable spectral features are of good rotational resolution as is noticeable from the indicated part of the spectrum which is represented enlarged in Fig. 2. The mixture of O$_3$–CF$_3$Br at a ratio of 1:9 was irradiated at a wavelength of 308 nm. The total cell pressure in this experiment was 200 Pa. The BrO($X\ ^2\Pi$) $2h\nu$ LIF signal was detected 2.5 μs after ozone photolysis. In using these parameters the maximum signal intensity was obtained.

From the experimental conditions a rough estimation of the BrO detection limit can be deduced. Taking into account the photolysis energy, the focal area, the O$_3$ absorption cross section and O(^1D) quantum yield at 308 nm, the upper limit for the initial BrO concentration generated in the O(^1D)+CF$_3$Br reaction is $2\cdot 10^{15}$ cm^{-3}. The signal-to-noise

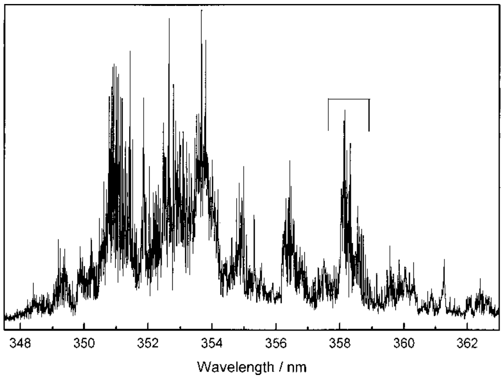

FIG. 1. Two-photon LIF spectrum of BrO obtained from the reaction of O(^1D) atoms with CF_3Br (180 Pa) O(^1D) atoms were prepared in the photodissociation of ozone (20 Pa) at 308 nm. The BrO product was observed 2.5 μs after ozone photolysis.

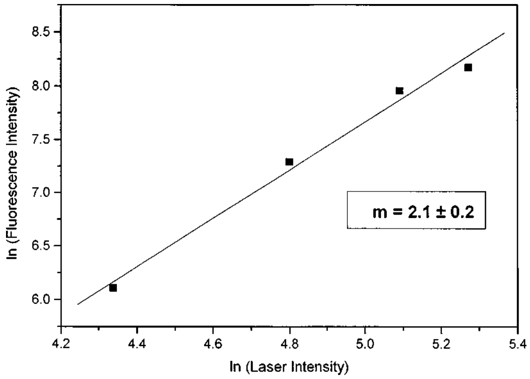

FIG. 3. Dependence of the BrO fluorescence signal intensity on the detection laser intensity at 358.2 nm indicating the observed LIF signal being the result of a two-photon excitation.

ratio was above 60:1 when the fluorescence signal was averaged over two lasershots. Given the detection volume of $3\cdot 10^{-4}$ cm^3 and with the assumption of a hundred populated states we expect a detection limit of $1.4\cdot 10^8$ BrO molecules per quantum state.

At the delay times between photolysis and detection used in the experiment diffusion processes were negligible; however, at longer delay times these processes have to be considered. Therefore, no decay rates for BrO were measured in this work.

As soon as the photolysis laser was blocked or fired after the detection laser BrO signals were not observable. To be sure that the fluorescence signals of BrO which are observed in the wavelength range between 348 and 363 nm are the result of a two-photon excitation, the logarithm of the fluorescence signal was plotted as a function of the logarithm of the detection laser pulse energy (Fig. 3). The slope of the linear fit is close to two as it is expected for two photon processes. As a consequence, the obviously radiative BrO electronic state attained in our experiment lies a hitherto uninvestigated energy region of $T_e = 56\,000$ cm^{-1}.

In addition to the BrO $A\ ^2\Pi$ ($T_e = 26\,098$ cm^{-1}) first excited electronic state, which is not suitable for LIF detection due to predissociation,[13] higher-lying electronic states of BrO known by now are the $E\ ^2\Sigma$ ($T_e = 64\,916$ cm^{-1}), $F\ ^2\Sigma$ ($T_e = 67\,420$ cm^{-1}) and G ($T_e = 70\,441$ cm^{-1}) states which had at first been observed by Duignan and Hudgens[7] by employing a three-photon REMPI detection scheme at wavelengths between 417 and 474 nm. In comparison with the $A\ ^2\Pi$ ($T_e = 31\,750$ cm^{-1}), $E\ ^2\Sigma$ ($T_e = 67\,323$ cm^{-1}), $F\ ^2\Sigma$ ($T_e = 70\,093$ cm^{-1}) and G ($T_e = 73\,600$ cm^{-1}) excited electronic states of ClO, the corresponding BrO states are all lower in energy. Hence, a similar behavior should be observed for the C states of BrO and ClO. Accordingly, our BrO two-photon LIF spectrum (Fig. 1) can only be rationalized with $C-X$ rovibronic progressions. Compared to the corresponding ($C\ ^2\Sigma, v=0 \leftarrow X\ ^2\Pi_\Omega, v, J$) two-photon LIF spectrum of the ClO radical[14] the BrO ($C \leftarrow X\ ^2\Pi_\Omega, v, J$) two-photon LIF spectrum is far more congested. This is not surprising considering the following facts. The rotational constants for BrO are smaller than for ClO leading to more populated states in the X state and to smaller distances within the rotational branches. Furthermore, the natural ratio of ^{35}Cl–^{37}Cl is 75.8:24.2, the natural isotope abundance of ^{79}Br–^{81}Br, however, is nearly equal. Thus, the number of rotational transitions is expected to be more than doubled. Whereas the respective $\Omega = 1/2$ spin–orbit subband of ClO($X\ ^2\Pi_\Omega$) does not overlap with other spin–orbit subbands in the ($C \leftarrow X$) two-photon LIF spectrum, this will be the case in the corresponding BrO spectrum due to the spin–orbit constant ($A = -968$ cm^{-1}) being comparable to the vibrational frequency ($\omega_e = 727$ cm^{-1}) for the BrO($X\ ^2\Pi_\Omega$) ground state. Moreover, ClO($C\ ^2\Sigma, v > 0 \leftarrow X\ ^2\Pi_\Omega, v$) transitions do scarcely appear in the ClO two-photon LIF spectra because of fast predissociation;[9,11] this is not necessarily the case for BrO.

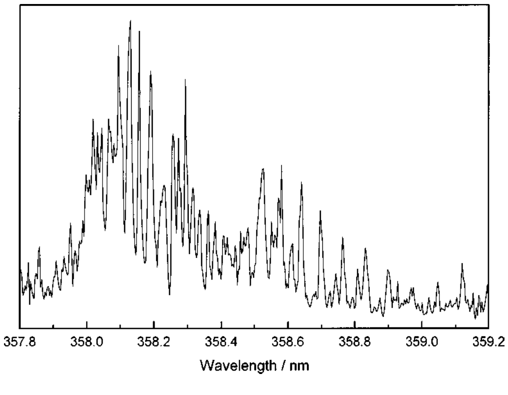

FIG. 2. Blow up of the experimental two-photon LIF ($C \leftarrow X\ ^2\Pi_\Omega, v, J$) spectrum of BrO taken from Fig. 1.

Despite the above described drawbacks preventing at present an unambiguous assignment of the BrO spectrum, we made an effort to simulate an apparent vibrational band of the BrO spectrum. We used the known constants for the BrO($X\ ^2\Pi, v=0, J$) states which were obtained by infrared measurements[15] and considered only the ^{79}BrO isotope. Given the above facts, the correspondence between measurement and calculated transition remained unsatisfactory. The spectroscopic constants estimated for the upper C state of BrO which were employed in the simulated ($C\ ^2\Sigma, v \leftarrow X\ ^2\Pi_{\Omega=3/2}, v=0, J$) transition were $B = 0.35$ cm^{-1}, $D = 5\cdot 10^{-7}$ cm^{-1}, $\gamma = 0.02$ cm^{-1}. In order to obtain a maximum correspondence between experiment and simulation, B was varied over a range of 0.33 and 0.37 cm^{-1}. From these values a bond length of $r = 190 \pm 6$ pm is calculated for the C state of BrO. In any case, the value of the rotational constant of the C state of BrO is, in contrast to ClO, smaller than the one for the X state. The BrO two-photon transitions observed in reaction (1) which are depicted in Fig. 1 were also observed from reaction (2). Given the exothermicity of both reactions and the manifold of transitions observed in our spectra, the BrO($X\ ^2\Pi$) products should be formed with vibrational excitation. At present an unambiguous assignment of the vibrational and rotational transitions occurring in the BrO($C - X\ ^2\Pi_\Omega, v, J$) two-photon LIF spectrum is not yet possible due to the spectroscopic properties of BrO described above. However, the problem caused by the isotope abundance can be overcome by mass selective REMPI time-of-flight investigations. Moreover, the assignment should be facilitated in taking jet-cooled BrO ($C - X$) spectra. Summarizing, nascent BrO products can now be analyzed on a state selective basis and, consequently, it becomes possible to elucidate the dynamics of reaction and dissociation processes involving BrO radicals.

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