Bromine Dioxide, OBrO: Spectroscopic Properties, Molecular Structure, and Harmonic Force Field**

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The halogen oxides show a great variation in structural parameters and other physical as well as chemical properties. Over a dozen chlorine oxides are known, many of them quite well characterized; fewer bromine oxides are known, and their properties are not as extensively studied.[1] Recently the chlorine and bromine oxides have attracted considerable attention because of their implication in reaction cycles leading to the destruction of atmospheric ozone. Of particular importance are the catalytic cycles involving ClO and BrO. Recently, bromine dioxide, OBrO, has been observed in the bromine sensitized photodecomposition of O_3.[2,3]

Bromine dioxide was first reported by Schwarz and Schmeißer as an egg-yellow deposit from a Br_2/O_2 discharge.[4] The stoichiometry was deduced by quantitative analysis, and the product, decomposed rapidly above 0°C. Later, Schmeißer and Jörger reported the same compound as a product of the Br_2 ozonolysis in cooled CCl_3F solution.[5] The Seppelt group, however, obtained single crystals of orange Br_2O_3[6] and colorless Br_2O_5[7] from that reaction but found no evidence for molecular OBrO. OBrO was detected during mass spectroscopic investigations of the O + Br_2 reaction system,[8] ESR studies of X-ray irradiated perbromates,[9] and UV/vis spectroscopic investigations of the' Br + O_3 reaction system.[2,3] The ν_1[10] and ν_3[10,11] stretching fundamentals were observed in Ar matrices.

We have observed the rotational spectrum of the triatomic

oxide OBrO in the millimeter- and submillimeter-wave regions using the spectrometer] described in ref. [12]. We report here the rotational and quartic centrifugal constants as well as the derived r_0 structure and harmonic force field.

The reaction products of an O_2 discharge plus Br_2 were condensed onto the wall of the microwave absorption cell at -20°C. After the flow of O_2 and Br_2 was stopped, spectra of the vapor were recorded while pumping on the condensate. The identity of the product on the walls is not clear. It might be OBrO, a more complex bromine oxide, or a mixture of oxides that decompose slowly to yield OBrO. At low temperatures (--20°C) and pressures (0.1 Pa) essentially all absorption features were due to OBrO, although weak features of BrO were also seen. The amount of OBrO increased at higher temperatures because of a larger vapor pressure or an enhanced decomposition of its precursor. The BrO/OBrO ratio also increased as well, possibly because of decomposition of OBrO. Strong aborptions of Br_2O were also seen at higher pressures (reduced flow rate) and higher temperatures.

The OBrO rotational spectrum is that of a C_{2v} molecule in the $^2B_1$ electronic ground state, as is that of OCl (). In general, each rotational transition is observable as a doublet of quartets. This is illustrated in Figure 1 for a transition having rather small splittings. The doublets indicate the presence of an unpaired electron, the quartets are due to one

nucleus with spin 3/2 (^{79}Br or ^{81}Br). A large number of lines has been observed resulting in the precise determination of rotational, centrifugal distortion, fine, and Br hyperfine structure constants. Rotational and quartic centrifugal distortion constants for the vibrational ground state are given in Table 1.

The rotational constants have been used to calculate the r_0 structural parameters of OBrO. They are given with data for related molecules in Table 2. The equilibrium (Y<,) structure of OBrO is not- precisely known. The r_e bond length and bond angle respectively are ca. 0.5 pm and 0.18° smaller than the r_0 parameters, as estimated from the changes of related molecules. The bond length in OBrO is substantially larger than in OClO, as expected. The difference is very similar to that between SeO_2 and SO_2. However, the bond angle in OClO is smaller than in SO_2, whereas the one in OBrO is slightly larger than in SeO_2.

The quartic distortion constants have been used to calculate the harmonic force field of OBrO. The force constants are also given in Table 2 together with those of OClO, SO_2, and SeO_2. The diagonal force constants f_r and f_α change from OClO to OBrO by shout. the same amount as from SO_2 to SeO_2.

'l'he fine and hyperfine (:c)]~st.tint s are in reasonable agreement with those from ESR studies. [9] Their detailed

discussion is beyond the scope of the present communication.

We have also observed the ν_3 mode of OBrO in the gas phase (Fig. 2). The Q-branch feature of $O^{79}BrO$ at 846.1 cm^{-1} and the isotopic shift of 2.4 cm^{-1} agree well with values from the force field (851.2 and 2.35 cm^{-1}) as does the position of ν_1 in an argon matrix (794.6 versus 794.1 cm^{-1} from ref. [10]). The calculated isotopic shift on ν_1 is 1.15 cm^{-1}; an observed shift of 2.9 cm^{-1} is more likely due to a matrix effect; see for example ref. [13], where this has been studied in detail for OClO. Although the bending mode has not yet been observed directly, our calculated value of 311 cm^{-1} for $O^{79}BrO$, is consistent with relative intensities observed for rotational transitions in the ground state compared to those in the ν_2 = 1 state (Fig. 1).

In conclusion, we have used the O + Br_2 reaction system to study the OBrO radical. The presence of a mixture of bromine oxides under certain conditions indicates complex secondary chemistry which may be of atmospheric importance. Work in our laboratory continues on the spectroscopy and kinetics of these interesting molecules.

Keywords: bromine dioxide, free radical, rotational spectroscopy, structure determination, force field

Summary: The unstable OBrO radical, which might play a role in atmospheric chemistry, has been observed in the gas phase over a solid product of the $O_3 + Br_2$ reaction. Under certain conditions BrO, OBrO, and Br_2O could be observed simultaneously.

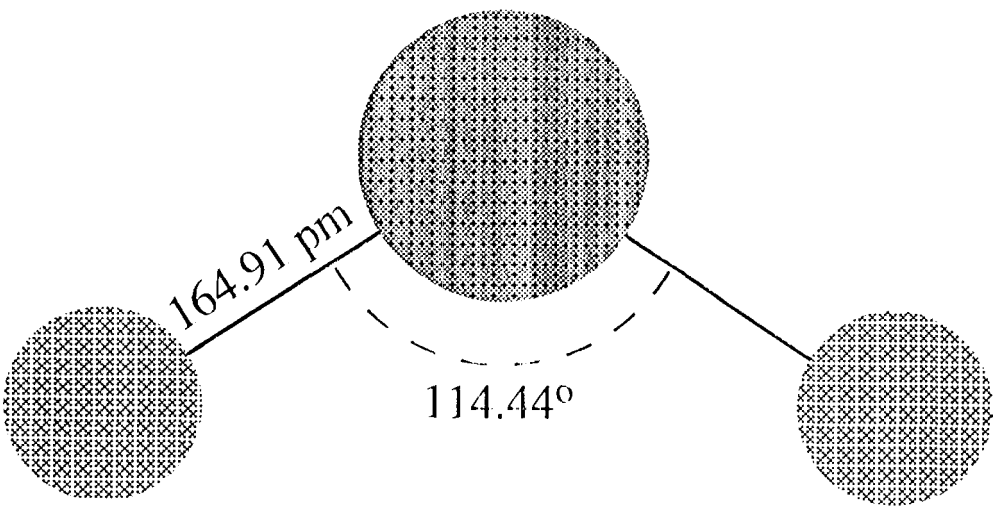

Fig. 1: Detail of the submillimeter spectrum of the bromine dioxide radical. The $31_{1,30} - 30_{2,29}$ transition of $O^{81}BrO$ in the ground vibrational state (full circles) and of $O^{79}BrO$ in the first excited bending mode (open circles) are indicated. In general each transition appears as a doublet of quartets; see text.

Fig. 2: The infrared spectrum of gaseous OBrO in the region of the ν_3 fundamental showing PQR branch structure (resolution: 1 cm^{-1}).

Table 1: Rotational (MHz) and quartic centrifugal distortion constants[a] (kHz) of OBrO in the ground vibrational state.

	$O^{79}BrO$	$O^{81}BrO$
A	28 024.517 86 (111)	27 824.891 27 (116)
B	8 233.172 65 (32)	8 233.254 58 (33)
C	6 345.433 14(32)	6335.136 67 (35)
D_J	7.134 86 (48)	7.124 76 (50)
D_{JK}	-70.692 5 (33)	-69.980 8 (33)
D_K	714.380 (27)	'/04.391 (23)
d_1	-2.637 543(124)	-2.642 155 (124)
d_2	-0.156 5 55 (53)	-0.156 80-/ (54)

[a] Numbers in paranthesis are two standard deviations in units of the last significant figures. Watson's S reduction is used in the representation I'.

Table 2: Structural parameters (pm, deg) and harmonic force constants (N m^{-1}) of OBrO in comparison with related compounds,

	OBrO [b]	OClO [a, c]	SeO_2 [a, d]	SO_2 [a, e]
r	164.91	146.984	160.176	143.080
α	114.44	117.403	113.83	119.329
f_r	530.5	711.0	705.7	3030.4
f_α	99.5	137.2	135.7	168.0
f_{rr}	-3.1	25.0	12.9	0.8
$f_{r\alpha}$	-4.1	2.7	13.8	28.7

[a] Equilibrium structure. [b] This work; r_0 structure.

[c] Refs. [14, 13]. [d] Refs. [15, 16]. [e] Refs. [17, 14].

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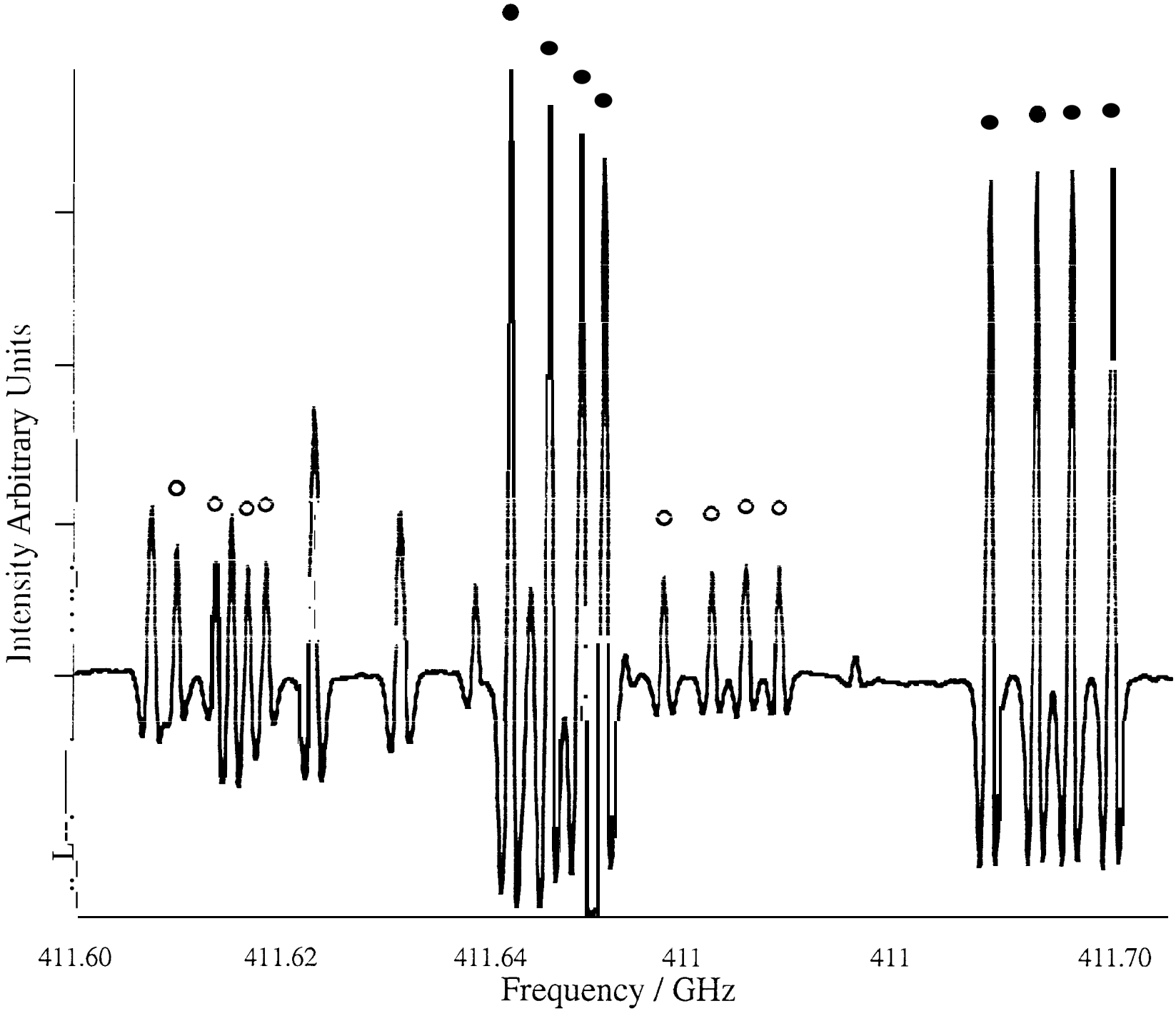
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411.64
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411
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Frequency / GHz
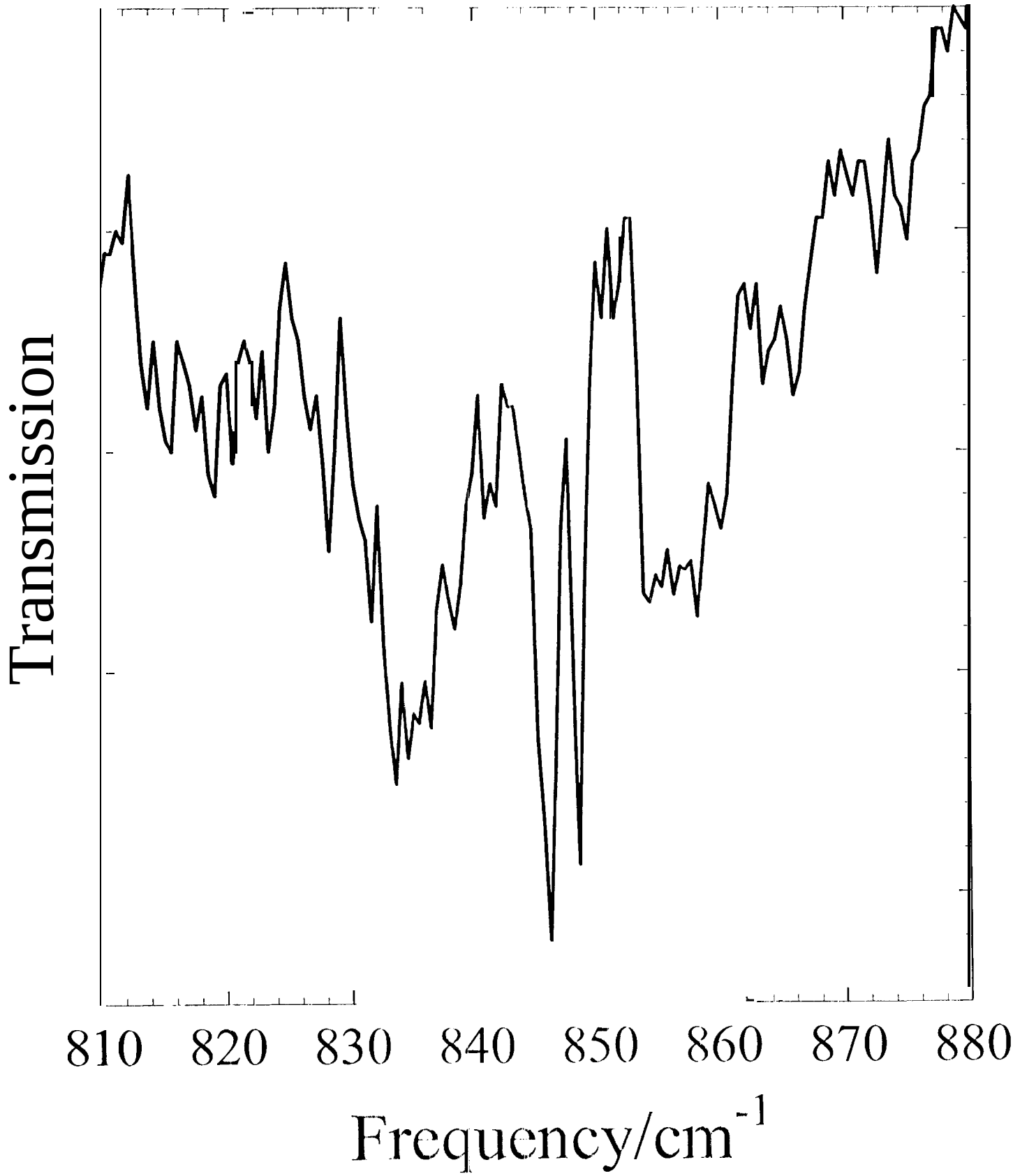
Figure 2