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The microwave spectrum of the cesium monoxide CsO radical

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The microwave spectrum of CsO has been observed and analyzed, not only in the ground vibrational state, but also in the v=1-3 excited vibrational states. The CsO radical was generated by the reaction of N₂O with Cs vapor, which was produced by the reaction of Li metal with CsCl at 500–530 °C. The observed spectra were found to conform to those expected for a $^{2}\Sigma$ diatomic molecule, thereby establishing the ground electronic state of CsO to be of ${}^{2}\Sigma$. The observed rotational and centrifugal distortion constants yielded the equilibrium bond length and the harmonic vibrational frequency to be 2.300 745 (16) Å and 356.78 (11) cm⁻¹, respectively, based on the Born-Oppenheimer approximation. A careful examination of the observed spectral pattern definitely concluded that the spin-rotation interaction constant was positive, at variance with the expectation from a simple ${}^{2}\Sigma/{}^{2}\Pi$ two-states interaction. This observation was interpreted by assuming positive contributions from higher excited electronic states which superseded a negative contribution from the ${}^{2}\Pi$ lowest excited state; the latter state was responsible for the large dependence of the spin-rotation interaction constant on the vibrational quantum number and was estimated from this vibrational dependence to be located at 1225 cm⁻¹ above the ground electronic state. In reverse to the spin-rotation splitting, the hyperfine splitting was found to increase with the vibrational excitation; in the v=3 state the hyperfine structure was found completely resolved. However, the hyperfine coupling constants did not vary much with the vibrational quantum number, namely the vibrational dependence of the hyperfine splitting was caused primarily by that of the spin-rotation splitting. The observed hyperfine interaction constants indicated that CsO was an ionic molecule. © 1999 American Institute of Physics. [S0021-9606(99)00845-4]

I. INTRODUCTION

Cesium monoxide is the last member of the series of alkali monoxides, which we have been investigating systematically by using microwave and infrared diode laser spectroscopy. We have already reported the results on LiO,^{1,2} NaO,³ and RbO,⁴ and Hirota⁵ has briefly described the spectroscopic information so far obtained on KO, RbO, and CsO in a review paper.

Very little has been known on the CsO radical in the gas phase. Sarkas *et al.*⁶ determined the A-X separation in CsO to be 0.135 ± 0.025 eV (1089 ± 202 cm⁻¹) by applying photodetachment spectroscopy to CsO⁻ and confirmed the ground electronic state of CsO to be of ${}^{2}\Sigma^{+}$. Spiker and Andrews^{7,8} observed the fundamental band of CsO isolated in a nitrogen and an argon low-temperature matrix at 314 and 322 cm⁻¹, respectively. They produced radicals by the reactions of cesium metal with N₂O and ozone in the matrices, respectively. Lindsay, Herschbach, and Kwiram⁹ reported the observation of electron spin resonance (ESR) spectra of CsO isolated in nitrogen, argon, or krypton matrices at 4 K. The production of the radical was similar to that used in the infrared studies.

Allison et al.^{10,11} and Langhoff et al.¹² performed ab ini-

tio calculations on CsO and other members of alkali monoxides. They reported the bond length and the vibrational frequency in addition to the ${}^{2}\Pi - {}^{2}\Sigma$ energy separation.

The present paper describes the microwave spectrum of CsO and reports the molecular constants derived from there.

II. EXPERIMENT

We generated cesium monoxide radicals by the reaction of N₂O with Cs vapor, which we produced by heating a mixture of lithium metal and CsCl in a stainless steel absorption cell. We continuously pumped dinitrogen monoxide gas through the cell at the pressure of 10–12 mTorr. Absorption lines which were presumably due to CsO radicals started to appear when the cell temperature reached 350 °C and they became strong at 500–530 °C. Lithium metal of 20 g lasted for 2 days.

The microwave spectrometer employed in the present study was identical to that used for RbO (Ref. 4) and was described in detail in Ref. 13.

III. OBSERVED SPECTRA

Search for the spectra of the CsO radical was initiated in the frequency region from 339 to 383.4 GHz, and several lines were observed and were tentatively assigned to the $N = 26 \leftarrow 25$, $27 \leftarrow 26$, and $28 \leftarrow 27$ transitions. Later the measurement was extended to lower frequency region in order to

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TABLE I. Part of the observed frequencies of rotational transitions of CsO in the v=0, 1, 2, and 3 (in MHz).

				v=0			v=1				
$N' \leftarrow N''$		$J' \! \leftarrow \! J''$		$F' \leftarrow F''$		obs	<i>o</i> - <i>c</i>	wt	obs	<i>o</i> – <i>c</i>	wt
9 8		8.5	7.5	12.0	11.0	119 779.752	0.128	1.00	119 108 007	0.051	1.00
				11.0	10.0	119 781.954	0.015	0.41	119 111.073	0.156	1.00
				10.0	9.0	119 783,195	0.030	0.36	119 113.316	0.044	0.32
				9.0	8.0	119 783.808	0.094	0.32	119 115.263	0.219	0.28
				8.0	7.0	119 783 808	0.094	0.28	119 115 263	0.219	0.24
				7.0	6.0	119 783 195	0.030	0.26	119 115 263	0.219	0.21
				6.0	5.0	119 781 954	0.015	0.24	119 113 316	0.044	0.19
				5.0	4.0	119 /01.951	0.015	0.20	119 115.516	0.011	0.17
		9.5	8.5	13.0	12.0	120 208.412	0.019	1.00			
				12.0	11.0	120 206.357	0.001	0.40	119 471.768	0.040	1.00
				11.0	10.0	120 205.356	0.036	0.36	119 469.889	0.112	1.00
				10.0	9.0	120 205.356	0.036	0.32	119 468.191	0.018	0.32
				9.0	8.0	120 205.356	0.036	0.29	119 468.191	0.018	0.29
				8.0	7.0	120 206.357	0.001	0.26	119 468.191	0.018	0.26
				7.0	6.0	120 207.380	0.086	1.00			
				6.0	5.0	120 208.929	0.037	1.00			
13	12	12.5	11.5	16.0	15.0	173 062.421	-0.089	0.42	172 077.807	0.010	1.00
				15.0	14.0	173 063.523	-0.056	0.39	172 079.333	0.067	1.00
				14.0	13.0	173 064.362	-0.034	0.36	172 080.398	0.050	1.00
				13.0	12.0	173 064.362	-0.034	0.33	172 081.112	0.038	0.33
				12.0	11.0	173 064.362	-0.034	0.30	172 081.112	0.038	0.30
				11.0	10.0	173 064.362	-0.034	0.28	172 081.112	0.038	0.28
				10.0	9.0	173 063 523	-0.056	0.26	172 079 739	0.004	1.00
				9.0	8.0	173 062.421	-0.089	0.24	172 077.178	0.089	1.00
		125	10.5	17.0	16.0	172 401 095	0.020	0.42	172 442 000	0.124	1.00
		15.5	12.3	17.0	15.0	173 491.083	0.029	1.00	172 443.900	-0.124	1.00
				16.0	15.0	173 490.003	-0.046	1.00	172 442.505	0.090	1.00
				15.0	14.0	1/3 489.338	-0.022	0.36	172 441.440	-0.262	0.36
				14.0	13.0	173 489.338	-0.022	0.33	172 440.686	0.118	0.33
				13.0	12.0	173 489.338	-0.022	0.31	172 440.686	0.118	0.31
				12.0	11.0				172 440.686	0.118	0.28
				11.0	10.0				172 440.686	0.118	0.26
				10.0	9.0	173 491.085	0.029	0.22	172 441.440	-0.262	0.24
17	16	16.5	15.5	20.0	19.0	226 293.483	-0.152	0.40	224 995.845	-0.089	1.00
				19.0	18.0	226 294.667	0.073	0.38	224 996.704	-0.083	0.38
				18.0	17.0	226 294.667	0.073	0.36	224 997.613	-0.024	0.35
				17.0	16.0	226 294.667	0.073	0.33	224 997.613	-0.024	0.33
				16.0	15.0	226 294.667	0.073	0.31	224 997.613	-0.024	0.31
				15.0	14.0	226 294.667	0.073	0.29	224 997.613	-0.024	0.29
				14.0	13.0	226 294.667	0.073	0.28	224 996.704	-0.083	0.28
				13.0	12.0	226 293.483	-0.152	0.26	224 995.264	-0.075	1.00
		17.5	16.5	21.0	20.0	226 720.701	-0.030	1.00	225 359.949	-0.214	1.00
				20.0	19.0	226 719.870	-0.060	0.38	225 359.130	-0.014	0.38
				19.0	18.0	226 719.870	-0.060	0.35	225 358.190	0.021	0.35
				18.0	17.0	226 719.870	-0.060	0.33	225 358.190	0.021	0.34
				17.0	16.0	226 719.870	-0.060	0.32	225 358.190	0.021	0.31
				16.0	15.0	226 719.870	-0.060	0.30			
				15.0	14.0				225 358.190	0.021	0.28
				14.0	13.0	226 721.145	0.150	1.00	225 359.130	-0.014	0.27
							v=2			v=3	
13	12	12.5	11.5	16.0	15.0	171 097.584	0.020	1.00	170 128.710	0.050	1.00
1.5				15.0	14.0	171 099.997	-0.008	1.00	170 132.806	-0.076	1.00
				14.0	13.0	171 101 932	-0.044	1.00	170 137 000	0.029	1.00
				13.0	12.0	171 103 419	-0.041	1.00	170 141 146	0.006	1.00
				12.0	11.0	171 104 348	0.005	0.52	170 145 602	-0.049	1.00
				11.0	10.0	171 104.340	0.005	0.52	170 140.002	0.049	1.00
				10.0	10.0	171 104.348	0.005	1.00	170 130.838	0.014	1.00
				9.0	9.0 8.0	171 096.137	-0.160	1.00	170 125.583	-0.151	1.00
		13.5	12.5	17.0	16.0	171 375 146	-0.123	1.00	170 258 005	-0.092	1.00
		13.5	14.3	16.0	15.0	171 272 817	-0.003	1.00	170 253 091	0.092	1.00
				15.0	14.0	171 270 022	0.005	1.00	170 255.981	0.020	1.00
				13.0	14.0	1/1 5/0.922	0.040	1.00	170 230.204	0.000	1.00

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							V = 0			v=1	
$N' \leftarrow N''$		$J' \! \leftarrow \! J''$		$F' \leftarrow F''$		obs	0-С	wt	obs	0-С	wt
				14.0	13.0	171 369.437	0.037	1.00	170 246.706	0.067	1.00
				13.0	12.0	171 368.285	0.012	0.54	170 242.963	0.008	1.00
				12.0	11.0	171 367.857	0.000	1.00	170 238.816	-0.045	1.00
				11.0	10.0	171 368.285	0.012	0.46	170 233.908	-0.073	1.00
				10.0	9.0	171 370.098	-0.033	1.00	170 227.942	-0.022	0.00
17	16	16.5	15.5	20.0	19.0	223 700.053	0.093	1.00	222 410.206	0.051	1.00
				19.0	18.0				224 413.013	0.056	1.00
				18.0	17.0	223 702.650	0.185	0.56	222 415.686	0.046	1.00
				17.0	16.0	223 703.604	0.009	0.35	222 418.266	0.022	1.00
				16.0	15.0	223 703.604	0.009	0.33	222 420.767	0.007	1.00
				15.0	14.0	223 703.604	0.009	0.31	222 422.977	-0.021	1.00
				14.0	13.0	223 702.650	0.185	0.44	222 423.850	0.007	1.00
				13.0	12.0	223 698.940	-0.138	1.00	222 407.877	-0.212	1.00
		17.5	16.5	21.0	20.0	223 974.384	-0.127	1.00	222 532.825	-0.119	1.00
				20.0	19.0	223 972.961	-0.007	1.00	222 530.128	-0.048	1.00
				19.0	18.0	223 971.794	0.050	1.00	222 527.650	0.015	1.00
				18.0	17.0	223 970.836	0.001	1.00	222 525.233	-0.001	1.00
				17.0	16.0	223 970.281	-0.025	0.35	222 522.910	0.003	1.00
				16.0	15.0	223 970.281	-0.025	0.33	222 520.647	0.010	1.00
				15.0	14.0	223 970.281	-0.025	0.31	222 518.657	0.062	1.00
				14.0	13.0	223 972.165	0.201	1.00	222 517.949	0.075	1.00

TABLE I. (Continued.)

confirm the rotational assignment. The observed spectral pattern completely conforms with that expected for a $^{2}\Sigma$ diatomic molecule.

Because the cesium atom consists of a single stable isotope with the nuclear spin quantum number I=7/2, the observed set of absorption lines was readily ascribed to the ground vibrational state. This set was accompanied by satellites, which were assigned to the excited vibrational states of v=1-3. Some additional lines were observed, which were probably due to the v=4 state, but they seemed to be much perturbed and we could not make any definite assignment for them. The observed rotational transitions are as follows:

 $v=0: N=7\leftarrow 6, 8\leftarrow 7, 9\leftarrow 8, 13\leftarrow 12, 14\leftarrow 13, 17 \leftarrow 16, 18\leftarrow 17, 19\leftarrow 18, 26\leftarrow 25, 27\leftarrow 26, and 28\leftarrow 27, v = 1: N=9\leftarrow 8, 13\leftarrow 12, 17\leftarrow 16, 18\leftarrow 17, 19\leftarrow 18, 26\leftarrow 25, 27\leftarrow 26, 28\leftarrow 27, and the lower-frequency spin component of 29\leftarrow 28, v=2: N=13\leftarrow 12, 14\leftarrow 13, 17\leftarrow 16, 19\leftarrow 18, 26\leftarrow 25, 27\leftarrow 26, 28\leftarrow 27, and 29\leftarrow 28, v=3: N=13\leftarrow 12, 14\leftarrow 13, and 17\leftarrow 16.$

Each rotational transition was found to consist of two groups of lines or, in a case of high-*N* transition, of a doublet, splitting being caused by the spin-rotation interaction. The spin splitting, which is about 430 MHz in the ground vibrational state, decreases rapidly with the vibrational quantum number *v*. Most of the spin components except for some high-*N* transitions of the ground vibrational state were observed further split into hyperfine components. The hyperfine splitting increases drastically with the vibrational quantum number; for the v=3 state even the $N=17 \leftarrow 16$ transition was completely resolved into hyperfine components. The analysis described below shows that the hyperfine coupling constants do not vary much with the vibrational quantum number and that the drastic increase of the hyperfine splitting

is primarily caused by the decrease of the spin-rotation interaction constant with vibrational excitation.

Table I includes some representative transitions observed for the four vibrational states. Figure 1 shows the $N = 13 \leftarrow 12$ transitions; the left and right insets depict, respectively, the lower- and higher-frequency spin components for v=0-2 and those for v=3 are reproduced in the upper and lower insets, respectively.

IV. ANALYSIS

The observed transition frequencies were subjected, separately for each vibrational state, to the least-squares analysis using the Hamiltonian for a ${}^{2}\Sigma$ diatomic free radical, which was identical to that used for RbO.⁴ The sign of the spin-rotation interaction constants required special attention; both the positive and negative signs yielded almost equally good fitting in spectral line frequency. However, as Fig. 2 clearly indicates, the hyperfine structure of the N=17 \leftarrow 16 transition in the v=3 state led us to favor the positive sign to the negative one; the positive and negative signs of the γ constant gave quite different intensity patterns and only a positive γ constant yielded the pattern in good agreement with the observed data. An analysis of this transition assuming the negative sign for γ resulted in the following constants: $\gamma = -144.3(2)$, $b_F = 432.4(60)$, and c = -267(19) in MHz, which may be compared with the positive case: $\gamma = 143.88(84)$, $b_F = 448.84(165)$, and c = 119.9(22) in MHz. A negative c constant implies that the unpaired electron occupies a p_{π} orbital, which is certainly not the case for the ground state of CsO. For the rest of the vibrational states v=0, 1, and 2 also, only the positive sign for γ led to reasonable sets of hyperfine constants.



FIG. 1. $N=13\leftarrow 12$ transitions of CsO in v=0, 1, 2, and 3. For the first three vibrational states the F_2 and F_1 components are shown in the left and right insets, respectively, whereas they appear in the upper and lower insets, respectively, for the v=3 state.

Table II summarizes molecular constants derived from the observed spectra.

V. DISCUSSION

The observed rotational spectra have established that the ground electronic state of CsO is of ${}^{2}\Sigma$, in agreement with the conclusion of previous studies.^{6,9} The observed data provide us with further information on the molecular structure of the radical, as listed below.

A. Molecular structure and vibrational frequency

The observed rotational constants were fitted to a power series in $(v + \frac{1}{2})$,

$$B_{\nu} = 6687.310(92) - 38.47(19)(\nu + \frac{1}{2}) - 0.258(46)(\nu + \frac{1}{2})^2,$$
(1)

where the values in parentheses denote standard deviations, which essentially represent the consistency among the four constants. The first term of the series corresponds to the equilibrium rotational constant B_e , provided that Born–



FIG. 2. Hyperfine patterns for the $N = 17 \leftarrow 16$ transition of CsO in the v = 3 state; the F_2 and F_1 spin components were displayed in the upper and lower insets, respectively. The observed intensity pattern agrees better with that calculated with a positive γ constant than with that obtained from a negative one.

Oppenheimer approximation holds for CsO. The difference between Y_{01} and B_e is 0.0095 MHz for CsF,¹⁴ and the correction for the breakdown of the Born–Oppenheimer approximation will not affect the results on CsO much. The equilibrium bond length r_e is thus readily calculated from the B_e constant to be 2.300745 (16) Å. This result may be compared with *ab initio* calculated lengths, 2.67 (Refs. 10, 11) and 2.425 Å.¹² A similar fit for the centrifugal distortion constants led to the following result:

$$D_{v} = 0.010\,456\,1(58) + 0.000\,022(12)(v + \frac{1}{2}) + 0.000\,020\,9(29)(v + \frac{1}{2})^{2},$$
(2)

again with standard deviations in parentheses. The equilibrium rotational constant B_e and the equilibrium centrifugal distortion constant D_e , the first term of Eq. (2), when inserted in the following conventional expression for the harmonic frequency ω_e :

$$\omega_e = (4B_e^3 / D_e)^{1/2},\tag{3}$$

result in $\omega_e = 356.78(11) \text{ cm}^{-1}$, which is somewhat larger than *ab initio* values, 286 (Refs. 10, 11) and 334 (Ref. 12) in cm⁻¹. For a reference, we cite Y_{10} and ω_e of CsF: 352.616 20(91) and 352.615 58(82) cm⁻¹.¹⁴

B. Lowest excited electronic state

We may anticipate to estimate the excitation energy of the lowest electronic state from the observed spin-rotation

TABLE II. Molecular constants of CsO (in MHz).^a

Constant	v=0	v=1	v=2	<i>v</i> =3
В	6 668.031 65(77)	6 628.964 9(14)	6 589.588 3(17)	6 549.490 9(20)
D	0.010 473 8(16)	0.010 532 9(28)	0.010 646 8(40)	0.010 789 6(40)
Н	0.000 000 003 8(10)	-0.000 000 005 0(17)	0.000 000 008 5(25)	
γ	432.263(48)	371.61(15)	286.02(16)	143.88(84)
γ_D	0.005 026(66)	0.007 45(17)	0.011 23(23)	0.018 7(26)
γ_H	$-0.000\ 000\ 043(39)$	0.000 000 168(95)	$-0.000\ 000\ 27(13)$	-0.0000048(35)
b	426.30(36)	427.3(22)	411.5(15)	408.9(15)
с	118.16(63)	111.9(37)	126.9(31)	119.9(22)
eQq	-23.4(33)	25.(11)	17.(15)	30.8(85)
T_{00}	0.069 9(96)	-0.079(12)	-0.015(14)	

^aValues in parentheses denote standard deviations and apply to the last digits of the constants.

interaction constant γ . However, as mentioned above, a careful examination of the observed spectra resulted in a positive sign for the constant. This observation precluded the possibility of simply applying the formula $\gamma = -4AB/\Delta E$ which was derived by a second-order perturbation treatment on a basis of the pure precession approximation.¹⁵ We have rather interpreted the observed γ constants to consist of at least two sources; the positive sign of the γ constants was ascribed to contributions of higher excited electronic states which superseded a negative contribution of the lowest excited II state. The marked dependence of the γ constant on vibrational excitation was presumed to be mainly caused by the interaction with the lowest II state.

In order to substantiate this interpretation, we have carried out a calculation using ab initio potential functions12 which were fitted to Morse potentials for ease of evaluating the Franck-Condon factors between the ground and the lowest excited Π states. We have then found that the observed decrease of the γ constant with the vibrational quantum number was reproduced when the excitation energy $-\Delta E$ of the Π state and the effective spin-orbit interaction constant A^{eff} were 1225 and -29.83 cm⁻¹, respectively, leaving a vibration-independent positive term γ_0 of 881.42 MHz as contributions from higher excited electronic states. Figure 3 compares the observed minus calculated spin-rotation interaction constants obtained by using this set [1] of $-\Delta E$, A^{eff} , and γ_0 with those derived from two other sets; [2] $-\Delta E$ = 1250 cm^{-1} , $A^{\text{eff}} = -32.80 \text{ cm}^{-1}$, and $\gamma_0 = +918.80 \text{ MHz}$, and [3] $-\Delta E = 1200 \text{ cm}^{-1}$, $A^{\text{eff}} = -27.06 \text{ cm}^{-1}$, and γ_0 = +846.31 MHz.

The excitation energy 1225 cm^{-1} of the Π state may be rationalized as follows. As mentioned above, we observed a few additional lines and suspected that they were assigned to the v=4 excited vibrational state; we could not have made any proper assignment for them presumably because they were subjected to severe perturbations. A plausible explanation for this observation is the interaction of the v=4 state with the Π electronic state. An equation derived by Pekeris,¹⁶

$$\omega_{e} x_{e} = B_{e} [(\alpha_{e} \omega_{e} / 6B_{e}^{2}) + 1]^{2}$$
(4)

led to $\omega_e x_e$ to be 1.432 cm⁻¹. The energy of the excited vibrational state measured from the ground state was thus calculated to be 353.92, 704.97, 1053.16, and 1398.49 cm⁻¹ for the v=1, 2, 3, and 4 states, respectively. Therefore, the

v=4 state can be buried in the manifold of the Π state. The excitation energy of 1225 cm⁻¹ we estimated agrees also with the result of Sarkas *et al.*,⁶ 1089±202 cm⁻¹.

The positive term γ_0 of 881.42 MHz may be accounted for by the contribution of an excited electronic state at 4539 cm⁻¹ above the ground state, provided that the effective spin–orbit coupling constant is 150 cm⁻¹.

C. Electronic structure

Lindsay *et al.*⁹ reported the hyperfine constants obtained from the ESR spectra; a = 139 G and $T_{\parallel} = 28$ G, which are converted to $b_F = b + c/3 = 390$ and c = 118 MHz to be compared with the present results, $b_F = 465.7(4)$ and c = 118.2(6) MHz.

As in the case of RbO,⁴ it is difficult to extract information on the unpaired electron from these hyperfine constants. When we compare the observed b_F constant with the atomic value 2467 MHz, as compiled by Morton and Preston¹⁷ for a 6s electron, the *s* character becomes 18.9%. However, we should use the value for a 5*s* electron, rather than for a 6*s* electron, and then the *s* character would reduce to 1% or so.



FIG. 3. Discrepancies between the observed and calculated spin-rotation interaction constants. The three sets [1], [2], and [3] of the calculated constants designated respectively by circles, squares, and triangles were obtained from the following parameters: [1] $-\Delta E = 1225 \text{ cm}^{-1}$, $A^{\text{eff}} = -29.83 \text{ cm}^{-1}$, and $\gamma_0 = +881.42 \text{ MHz}$, [2] $-\Delta E = 1250 \text{ cm}^{-1}$, $A^{\text{eff}} = -32.80 \text{ cm}^{-1}$, and $\gamma_0 = +918.80 \text{ MHz}$, and [3] $-\Delta E = 1200 \text{ cm}^{-1}$, $A^{\text{eff}} = -27.06 \text{ cm}^{-1}$, and $\gamma_0 = +846.31 \text{ MHz}$.

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The positive sign of the *c* constant is consistent with the electronic state being of ${}^{2}\Sigma$. It is, however, not easy to estimate the spin density from this constant.

The Cs nuclear quadrupole coupling constant is -23.4 (33) MHz in the ground vibrational state and changes its sign in the excited vibrational states; +25 (11) for v=1, +17 (15) for v=2, and +30.8 (85) MHz for v=3. These data indicate that the *eQq* constant of CsO is quite close to zero, suggesting that CsO is an ionic radical, as expected. The nuclear quadrupole coupling constant is 1.2452 (18) MHz in CsF,¹⁸ which is known as a typical ionic molecule.

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